

The Synthesis and Characterization of Monomeric Etherified Methylolated Melamines Using Gel Permeation Chromatography and Proton Magnetic Resonance Spectroscopy

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Synopsis

A series of monomeric etherified methylolated melamines were prepared and characterized by proton magnetic resonance spectroscopy and gel permeation chromatography. Gel permeation chromatographic analysis permits a rapid and accurate determination of the monomer and polymer content of the products. Proton magnetic resonance spectroscopy permits the qualitative identification of the etherifying alcohols and a quantitative estimation of the alkoxy groups present. The molar ratios of alcohols necessary to produce products having specific alkoxy contents are presented graphically.

INTRODUCTION

Melamine-formaldehyde resins are used as crosslinking agents in a wide variety of protective coatings. For most commercial applications, polymeric melamine-formaldehyde resins give the optimum coatings characteristics. With the advent of the electrodeposition process, renewed interest in low molecular weight melamine resins has emerged. This is primarily due to their dispersion characteristics in water and favorable migration rates under an electrical potential.¹⁻⁴

Numerous chemical and instrumental techniques have been described for the qualitative and quantitative analysis of melamine-formaldehyde resins.⁵⁻¹⁴ Very little information exists in the literature on the use of proton magnetic resonance spectroscopy and gel permeation chromatography for the characterization of monomeric and polymeric etherified methylolated melamines.^{15,16}

The present investigation was undertaken with the following objectives:

1. To prepare monomeric etherified methylolated melamines to be used as analytical standards.
2. To qualitatively identify etherified methylolated melamines from their proton magnetic resonance spectrum.

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3. To quantitatively determine the alkoxy content of the etherified methylolated melamines.

4. To ascertain the ratios of alcohols which must be charged to a reaction vessel to yield a product having specific alkoxy contents.

INSTRUMENTAL

The proton magnetic resonance spectra were obtained using a 60-MHz Jeolco C-60H spectrometer, operated in the field sweep mode at ambient temperature. The monomeric etherified methylolated melamines were examined as 10% solutions in carbon tetrachloride using tetramethylsilane (TMS) as an internal reference.

The gel permeation chromatograms were obtained using a Waters Associates Model 100 gel permeation chromatograph modified with an R-4 optical system. Analyses were performed using four columns in series having pore sizes of 800, 250, 100, and 45 Å as designated by the manufacturer. The column set had a plate count of 750 plates/ft using trichlorobenzene as the completely permeable solute. The columns were operated at ambient temperature using freshly distilled tetrahydrofuran as the eluting solvent. The degasser was operated at 55°C.

Gas-chromatographic analyses were performed using a Hewlett-Packard Model 5756 gas chromatograph equipped with flame ionization detectors. Separations were performed using a 20 ft \times $\frac{1}{8}$ in. column of 20% DC-401 silicone gum on 60-80 mesh Gas Pak WAB, operated at 100°C and a flow rate of 10 ml/min. Hydrogen and air flow rates were optimized for maximum detector response. The injection port and flame ionization detector were operated at 250°C. Peak areas were determined using a disc integrator.

EXPERIMENTAL

Preparation of Hexamethylol Melamine

Paraformaldehyde (450 g, 15.0 moles), water (500 g), and sodium carbonate (2.0 g) were charged to a flask equipped with a stirrer, thermometer, nitrogen purge, reflux condenser, and heating mantle. Stirring was initiated and the temperature slowly raised to 80°C. After a clear solution was obtained, the reaction mixture was slowly cooled to 60°C, and the pH was adjusted to 8.0 using sodium carbonate or acetic acid. Melamine (189 g, 1.5 moles) was then added over 60 min to avoid an exotherm. A flocculant white precipitate began to appear almost immediately. The reaction mixture was allowed to cool to room temperature, and the precipitate was removed by filtration. The precipitate was repeatedly redispersed in water, washed, and filtered until the odor of formaldehyde was removed. In some preparations this required as many as 20 washings.

Preparation of Etherified Methoylated Malamines

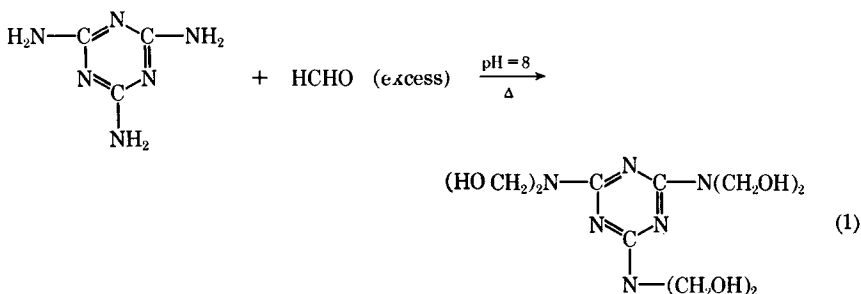
Hexamethylol melamine (30.6 g, 0.10 mole) and the appropriate alcohol or mixture of alcohols (10 moles) were charged to a flask equipped with stirrer, thermometer, reflux condenser, and heating mantle. The pH of the reaction mixture was adjusted to 1.5 using sulfuric acid, and the temperature was slowly raised to 40°C. The reaction mixture was kept at 40°C for 2 hr and then allowed to cool slowly to room temperature. The solution was then adjusted to a pH of 8 using potassium hydroxide, and the salt was removed by filtration. The unreacted alcohol was removed at room temperature and 0.1 mm pressure.

Determination of Alkoxy Content Using Alcohol Exchange

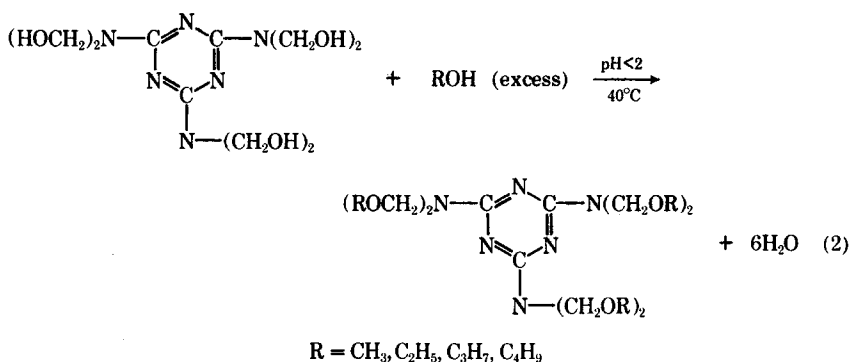
The type and amount of alkoxy groups in the etherified methylolated melamines can be determined by alcohol exchange with 2-ethylhexanol. Approximately 0.200 g of the etherified methylolated melamine is placed in a 250-ml Erlenmeyer flask equipped with a Claisen distilling head and receiver. Twenty-five milliliters of reagent-grade 2-ethylhexanol are added. The apparatus is placed on a combination magnetic stirrer-hot plate, stirring is begun, and the contents are brought to reflux. Refluxing is allowed to continue for 1 hr. The apparatus is then wrapped in aluminum foil, and the temperature of the hot plate is increased. Approximately 15 ml of material is allowed to distill into the receiver. An internal standard is added, and the amount of the exchanged alcohols is determined by gas chromatography.

RESULTS AND DISCUSSIONS

The reaction of melamine with formaldehyde to form hexamethylol-melamine is shown in eq. (1):



Failure to remove all excess formaldehyde after reaction made it impossible to prepare monomeric etherified products according to eq. (2):



In the presence of excess formaldehyde and at elevated temperatures, complex polymeric products may form.¹⁷⁻¹⁹

Figure 1 gives the gel permeation chromatogram of the methoxylated products prepared from two batches of hexamethylolmelamine. In the chromatogram, molecular size increases from left to right. Run #1 illustrates the effect of high etherification temperature and a single washing of the hexamethylolmelamine to remove excess formaldehyde. This reaction formed a large amount of polymeric species. Due to the insolubility of hexamethylolmelamine in solvents applicable to gel permeation chroma-

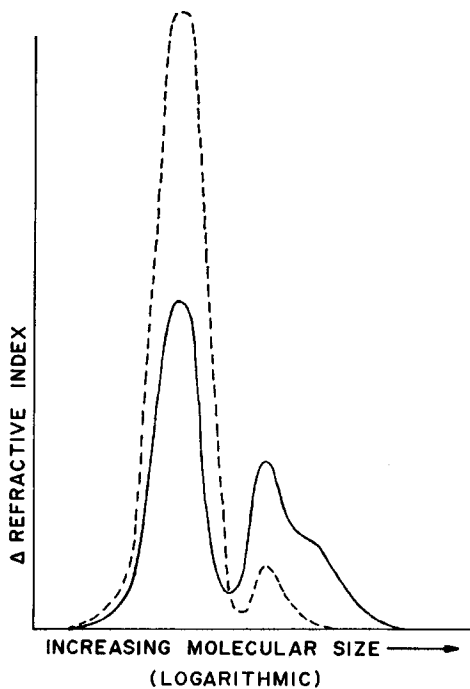


Fig. 1. Gel permeation chromatogram of methoxylated products from two batches of hexamethylolmelamine.

tography, the molecular size prior to etherification could not be determined. Run #4 was prepared with thoroughly washed hexamethylolmelamine and etherified at low temperature with a large excess of alcohol. In this case, a predominantly monomeric product resulted.

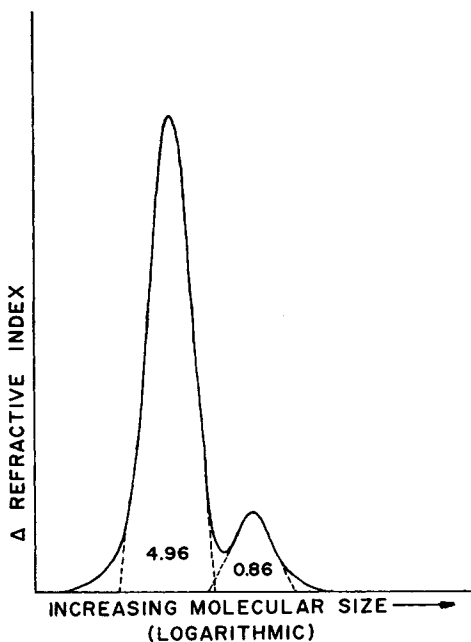


Fig. 2. Gel permeation chromatogram of methoxylated hexamethylolmelamine, illustrating calculation of monomer and polymer content.

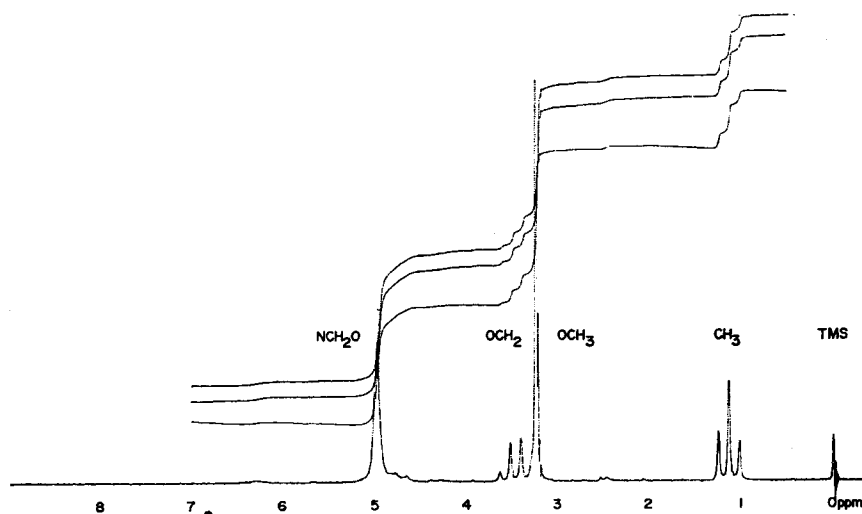


Fig. 3. Proton magnetic resonance spectrum of hexamethylolmelamine etherified with a 1:1 molar ratio of methanol and ethanol.

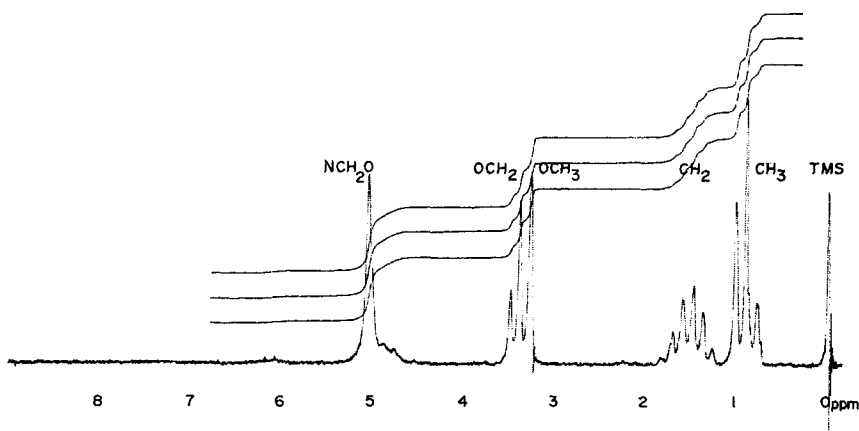


Fig. 4. Proton magnetic resonance spectrum of hexamethylmelamine etherified with a 1:9 molar ratio of methanol and *n*-butanol.

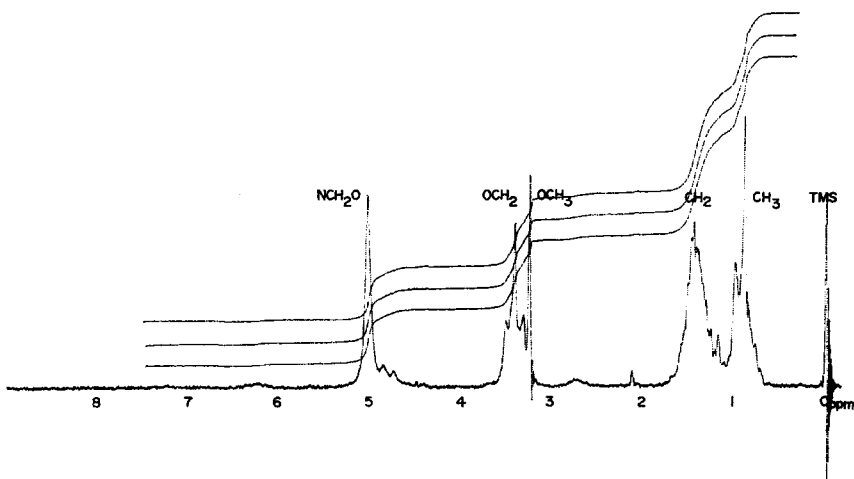


Fig. 5. Proton magnetic resonance spectrum of hexamethylmelamine etherified with a 1:9 molar ratio of methanol and *n*-butanol.

Figure 2 indicated the molecular size distribution of a typical etherified product formed in this series. The amounts of monomer and polymer are determined by measuring the areas of the corresponding peaks in the chromatogram. The amount of one component is then calculated by internally normalizing the peak areas. For several of the etherified methylolated melamines, the separated components were collected and weighed. The values for the monomeric and polymeric species were the same as those calculated using the peak areas in the chromatogram.

Figures 3 to 7 are the proton magnetic resonance spectra of typical etherified methylolated melamines. The band at 0 ppm is the internal reference, TMS. The resonance band near 5 ppm is due to the protons of

the N—CH₂—O group. Several less intense bands also appear in this region.

The multiple resonance near 5 ppm indicates the complexity of these systems. Monomeric etherified methylolated melamines should exhibit a single line for the N—CH₂—O protons. Polymeric formaldehyde species and polymeric species containing an N-CH₂-N group will also give bands in this region. Since these additional bands are not completely characterized at this time, determination of the extent of polymerization using proton magnetic resonance spectroscopy cannot be performed.^{15,20} Character-

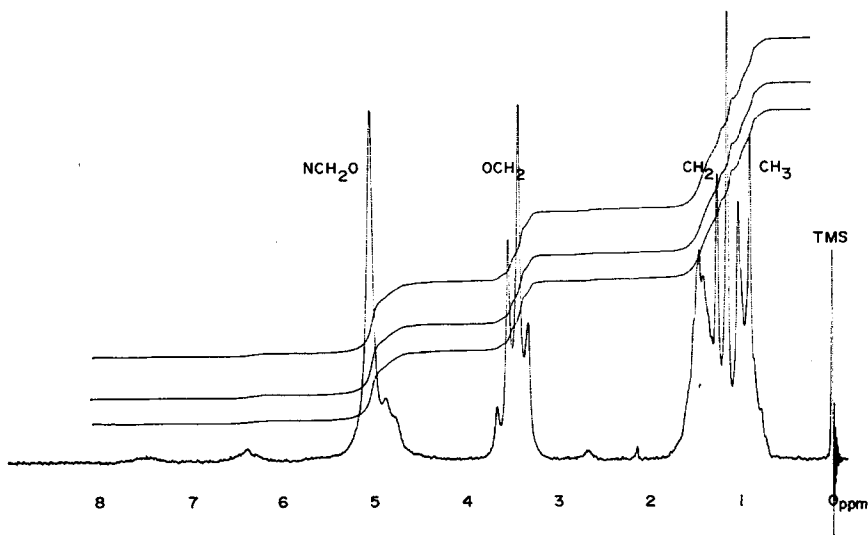


Fig. 6. Proton magnetic resonance spectrum of hexamethylolmelamine etherified with a 1:3 molar ratio of ethanol and *n*-propanol.

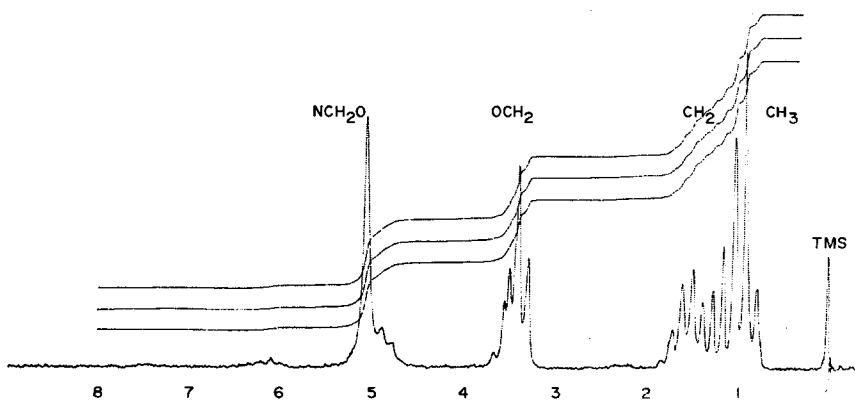


Fig. 7. Proton magnetic resonance spectrum of hexamethylolmelamine etherified with a 1:1 molar ratio of ethanol and *n*-butanol.

TABLE I
Per Cent Monomer Determined by Gel Permeation Chromatography*

Initial composition, mole-%	Monomer, mole-%
MeOH 25, EtOH 75	85
MeOH 50, EtOH 50	86
MeOH 75, EtOH 25	76
MeOH 10, BuOH 90	94
MeOH 25, BuOH 75	94
MeOH 50, BuOH 50	93
MeOH 75, BuOH 25	82

* MeOH, Methanol; EtOH, ethanol; BuOH, butanol.

ization of these bands may be possible using a spectrometer having a higher magnetic field strength.

The monomeric and polymeric composition for some of the systems studied as determined by gel permeation chromatography, is given in Table I.

The nuclear magnetic resonance spectra clearly distinguish the alcohols used during the etherification process. The resonance bands at 3 and 4 ppm are due to the protons on the α -carbon of the alcohols. The bands in the 1- to 2-ppm region are associated with proton resonances of the CH_2 and CH_3 groups in the alcohol that are adjacent to carbon atoms only.

TABLE II
Alkoxy Contents of Etherified Methylolated Melamines Using
Proton Magnetic Resonance Spectroscopy and Gas Chromatography*

Initial composition, mole-%	Alkoxy content, mole-%	
	Proton magnetic resonance	Gas chromatography
MeOH 25, EtOH 75	MeO 40	—
50, 50	67	MeO 65
75, 25	85	85
MeOH 10, PrOH 90	MeO 20	—
25, 75	41	—
50, 50	60	MeO 62
75, 25	80	83
MeOH 10, BuOH 90	MeO 19	MeO 21
25, 75	35	—
50, 50	65	—
75, 25	87	—
EtOH 10, PrOH	EtO 7	EtO 9
25, 75	27	—
50, 50	37	—
EtOH 10, BuOH 90	EtO 14	EtO 11
50, 50	54	—

* MeOH, Methanol; EtOH, ethanol; PrOH, propanol; BuOH butanol; MeO, methoxy; EtO, ethoxy.

The splitting of the resonance bands within each region is due to spin-spin splitting of the adjacent protons. These spin-spin splitting patterns may be used to characterize the alcohol or alcohols used for etherification. When a mixture of alcohols was used, the spin-spin splitting patterns overlap one another.

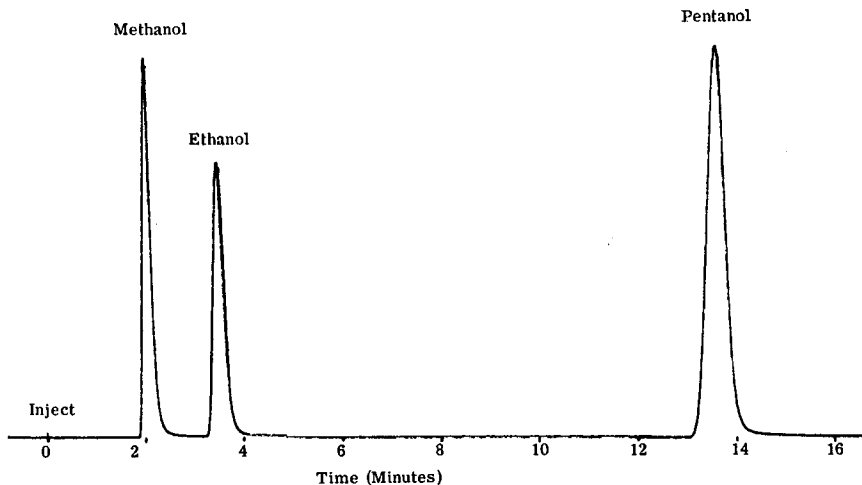


Fig. 8. Gas chromatogram of exchanged alcohols and internal standard.

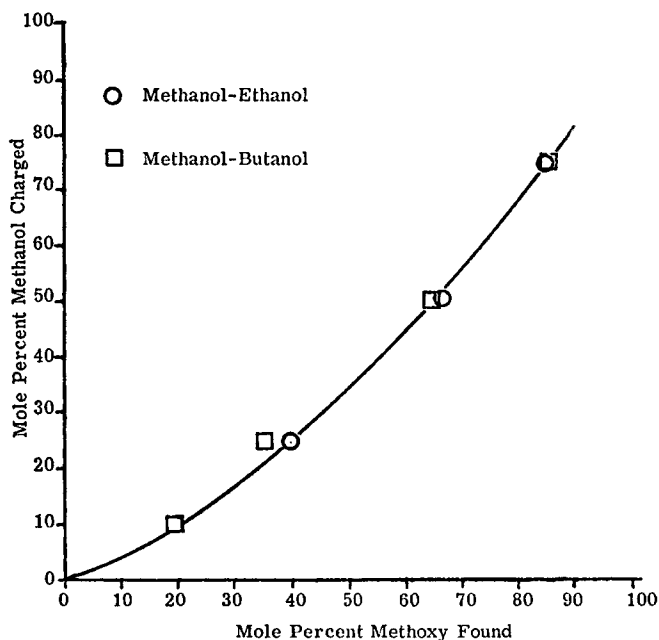


Fig. 9. Graph of alcohol charged vs. alkoxy content of product.

The ratio of the integrated areas of the resonance bands is related to the molar ratio of the number of protons of one type within the molecule. In preparations where more than one alcohol was used, the molar percentages of the alcohols can be determined from the integrated proton magnetic resonance spectrum. Details of the calculation procedure are given in the Appendix.

The molar amounts of alkoxy groups in the products were also determined using the established method of alcohol exchange and gas chromatography. A typical chromatogram of the distilled alcohols and internal standard is shown in Figure 8. The details of the calculations are given in the Appendix. The molar percentages of the alkoxy groups present in the etherified methylolated melamines are given in Table II. In all cases, the values obtained by proton magnetic resonance spectroscopy and alcohol exchange agree within a few per cent. Since the proton magnetic resonance method is considerably easier and less time consuming, it is the preferred technique for this analysis.

It is known that the molar ratio of alcohols charged during the etherification of hexamethylolmelamine is not the same as the alkoxy contents of the products. This is illustrated in Figure 9, where the mole-% alcohol charged to the reactor is plotted against the % alkoxy in the product. In all cases, methoxylation proceeds faster than ethoxylation, propoxylation, or butoxylation, as one would expect. Using graphs similar to that of Figure 9, one can determine the ratio of alcohols which must be charged to produce products having specific alkoxy contents.

Appendix

The calculations for computing the molar percentages of the etherifying alcohols are illustrated in the following example:

System: methoxylated-ethoxylated methylolated melamine

	Protons		
	$\text{—N—CH}_2\text{—O—}$	$\text{—O—CH}_2\text{—,}$ —O—CH_3	—CH_3
Chemical shift, ppm	5	3.5	1.1
Integrator units	38.0	52.6	8.5

The resonance at 1.1 ppm is a function of only the ethyl ether present in the molecule. The integral per proton of the ethyl group can be calculated from this datum in the following way: 8.5 integrator units \div 3 protons = 2.8 integrator units per proton. The resonance at 3.5 ppm is due to both methoxy and ethoxy groups. The integral per proton for the ethoxy groups is known, and the contribution to this band due to O—CH₂ of the ethoxy groups can be calculated (2.8 integrator units per proton \times 2 protons = 5.7 integrator units). The remainder of the integral (52.6 units $-$ 5.7 units = 46.9 units) is due to the protons on the methyl ether. The integrator units per proton for the methoxy group is then 46.9 integrator units \div 3 protons = 15.6 integrator units per proton. The mole percentages of methoxy and ethoxy in the molecule can be calculated in the following manner:

$$\frac{\left(15.6 \frac{\text{units}}{\text{OCH}_3 \text{ proton}}\right)}{\left(15.6 \frac{\text{units}}{\text{OCH}_3 \text{ proton}}\right) + \left(2.8 \frac{\text{units}}{\text{OCH}_2 \text{ proton}}\right)} (100) = 84.7\% \text{ methoxy}$$

The molar percentage of ethoxy groups is then 100%–84.7% methoxy = 15.3% ethoxy.

Knowing the integral per proton for the methoxy and ethoxy groups, the total integral for the —N—CH₂—O— protons can be calculated, assuming complete etherification. In this example, the integrator units for the N—CH₂—O protons should be 36.8 units (2 × 2.8 + 2 × 15.6 = 36.8). The measured value was 38.0 integrator units. The larger value found can be attributed to the etherification of polymeric melamine–formaldehyde species.

The weight percentages of the etherifying alcohols from the alcohol exchange reaction are calculated using the equation:

$$\%A = \frac{K_A \cdot A_A \cdot G_P \cdot 100}{K_P \cdot A_P \cdot W_s}$$

where %A = per cent of respective alcohol in resin, K_A = relative response factor of respective alcohol, A_A = area of the respective alcohol peak in the gas chromatogram, G_P = grams of internal standard (*n*-pentanol) added, K_P = relative response factor of *n*-pentanol (set equal to 1.00), A_P = area of the *n*-pentanol peak in the gas chromatogram, and W_s = weight of sample in grams.

Relative response factors are:

Alcohol	Relative response factor
Methanol	3.78
Ethanol	2.27
<i>n</i> -Propanol	1.71
<i>n</i> -Butanol	1.27

Duplicate determinations should agree within ±2% relative.

These data can then be used to calculate the molar percentages of the etherifying alcohols by obtaining the mole fraction of each alcohol and normalizing to 100%.

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