

The Analysis of Rigid Polyurethanes by Chemical Ionization Mass Spectrometry

N. A. MUMFORD*, D. A. CHATFIELD, and I. N. EINHORN,
*Flammability Research Center, University of Utah, Research Park, Salt
Lake City, Utah 84108*

Synopsis

Methods for the elucidation of the chemical components of polyurethane foams are described. Foam samples of 50 mg were hydrolyzed in aqueous base and the resulting mixture of polyols and polyamines was analyzed by chemical ionization mass spectrometry (CI-MS) and high-pressure liquid chromatography (HPLC). The aromatic polyamines, which were separated by HPLC, produced few fragment ions under methane chemical ionization and were identified without difficulty. Each propoxylated homolog in the mixture of polyols was detected by CI-MS techniques, and approximate molecular weight profiles are presented for each polyol studied. Chemical ionization spectra are listed for samples of standard polyols and of base-hydrolyzed isocyanates. The hydrolysis products from urethane foam formulations were easily related to the standard compounds via CI-MS. These methods should be applicable to polymeric materials containing urethane, urea, and ester linkages.

INTRODUCTION

The polyurethanes remain among the most versatile of all polymer systems with commercial applications in such varied areas as flexible and rigid urethane foams, elastomers, coatings, adhesives, and films. Recent work in our laboratory has been concerned with the chemical identification of urethane foams and the compounds produced from thermal degradation.¹ The nature of this work requires a knowledge of the chemical structures of the component parts of the polyurethane foams, and this information is not always made available by the manufacturer.

Numerous techniques for the identification of polyurethanes and their component parts have appeared in the literature. The most widely used technique is infrared (IR) spectroscopy.²⁻⁴ In several publications thermal analysis has been used to compare foams containing different formulations.^{5,6} Another procedure describes how samples can be reproducibly pyrolyzed and the volatile degradation products analyzed by gas-chromatographic (GC) techniques.⁷ A more thorough analysis, which involves fragmentation of the urethane into a polyol fraction and an amine fraction, has recently been reported.^{8,9} Dawson has published a comprehensive and detailed report on urethane foam identification that utilized sample hydrolysis followed by a lengthy extraction procedure to separate the components.¹⁰

This paper presents a simple and reliable method for the analysis of the component parts of rigid polyurethane foams. In this procedure foam samples

* To whom inquiries should be addressed at Research and Development Laboratories, Thiokol Corporation, Box 524, Brigham City, Utah 84302.

are hydrolyzed and the amine and polyol fractions are identified by chemical ionization-mass spectrometry (CI-MS). This method requires samples less than 50 mg and can be used to measure the ratios of homologs in the isocyanate fraction and the number of propoxylated components in the polyol fraction. This technique may be extended to the identification of the component parts of any polyester, polyurea, or polyurethane material.

TABLE I
Foam Sample Formulations

Component	Parts by weight
Foam 1	
Poly(methylenephenyl isocyanate) 1.05 Index (PAPI 135, Upjohn)	100.0
Propoxylated polyol (TP-340, Wyandotte)	70.2
Silicone surfactant (L-520, Union Carbide)	0.8
Trichlorofluoromethane (R-11B, Dupont)	19.7
Triethylenediamine (Dabco-33-LV, Houdry)	2.6
Foam 2	
Poly(methylenephenyl isocyanate) 1.05 Index (Mondur MR, Mobay)	100.0
Propoxylated polyol (RA-800, Dow)	48.5
Silicone surfactant (L-520, Union Carbide)	2.9
Trichlorofluoromethane (R-11B, Du Pont)	23.6
Fire retardant (Fyrol CEF, Stauffer)	25.0
Foam 3	
Poly(methylenephenyl isocyanate) 1.05 Index (PAPI 135, Upjohn)	100.0
Propoxylated polyol (Poly-G 531S, Olin)	75.1
Silicone surfactant (DC-193, Dow Corning)	1.5
Trichlorofluoromethane (R-11B), Dupont)	29.3
Amine catalyst (Polycat 8, Abbott)	3.8
Foam 4	
Poly(methylenephenyl isocyanate) 1.05 Index (PAPI 135, Upjohn)	100.0
Propoxylated polyol (Poly-G 530SA, Olin)	75.1
Silicone surfactant (DC-193), Dow Corning)	1.5
Trichlorofluoromethane (R-11B, Dupont)	28.9
Amine catalyst (Polycat 8, Abbott)	1.5

TABLE II
The Methane CI Mass Spectrum of the Hydrolyzate from 2,4-Toluene Diisocyanate

<i>m/e</i>	Relative intensity	Tentative assignment
122	20	M^+
123	100	$(M + 1)^+$
124	8	
151	31	$(M + 29)^+$
163	5	$(M + 41)^+$

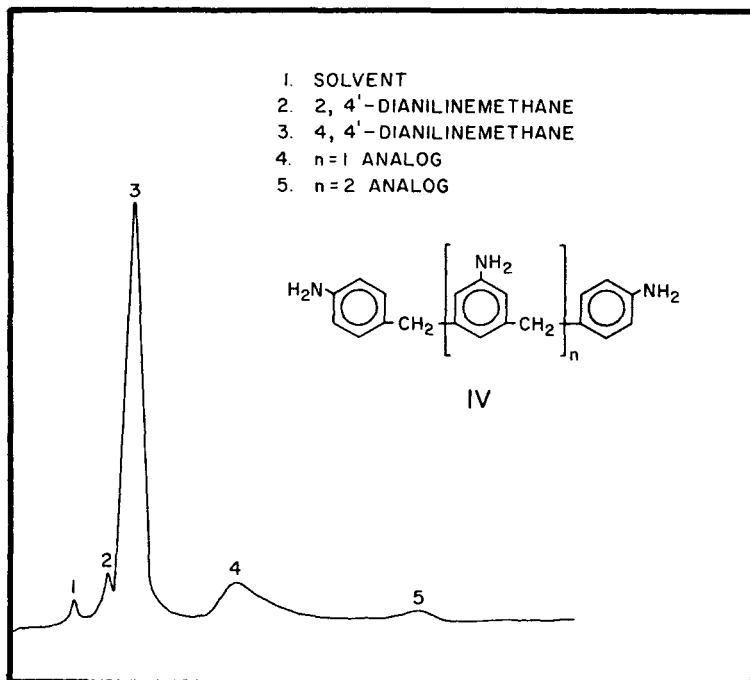
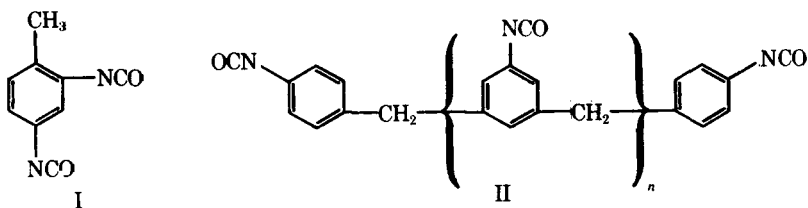


Fig. 1. HPLC trace of the hydrolysis products of poly(methylenephényl isocyanate) (IV).

EXPERIMENTAL

Amine and Polyol Standards

The aqueous base hydrolysis (*vide infra*) of selected isocyanates was used to prepare a set of five standard amines. These amines were obtained from the following isocyanates: 2,4-toluene diisocyanate (I) (Mondur TDS, Mobay); methylenedi-*p*-phenylene diisocyanate (II, $n = 0$) (Matheson, Coleman, and Bell); and poly(methylenephényl isocyanate) (II, average $n = 0.5$), (Mondur MR, Mobay):



Hydrolysis of I (abbreviated TDI) and II (known as MDI if $n = 0$ and poly-MDI

TABLE III
 The Methane CI Spectra of the Aromatic Amines in Compound IV

Compound	<i>m/e</i>	Relative intensity	Tentative assignment
2,4'-Dianiline methane, IV, <i>n</i> = 0	106	53	C ₇ H ₈ N, loss of C ₆ H ₇ N from <i>m/e</i> 199
	198	20	M ⁺
	199	100	(M + 1) ⁺
	200	16	
	227	6	(M + 29) ⁺
	239	4	(M + 41) ⁺
4,4'-Dianiline methane, IV, <i>n</i> = 0	106	37	C ₇ H ₈ N, loss of C ₆ H ₇ N from <i>m/e</i> 199
	107	3	
	198	22	M ⁺
	199	100	(M + 1) ⁺
	200	16	
	227	20	(M + 29) ⁺
Amine from Poly-MDI, IV, <i>n</i> = 1	106	5	C ₇ H ₈ N, loss of C ₁₃ H ₁₄ N ₂ from <i>m/e</i> 304
	211	63	C ₁₄ H ₁₅ N ₂ , loss of C ₆ H ₇ N from <i>m/e</i> 304
	212	10	
	302	9	
	303	26	M ⁺
	304	100	(M + 1) ⁺
	305	13	
	332	3	(M + 29) ⁺
	344	3	(M + 41) ⁺
Amine from Poly-MDI, IV, <i>n</i> = 2	106	14	C ₇ H ₈ N, loss of C ₂₀ H ₂₁ N ₃ from <i>m/e</i> 409
	211	85	C ₁₄ H ₁₅ N ₂ , loss of C ₁₃ H ₁₄ N ₂ from <i>m/e</i> 409
	212	12	
	316	86	C ₂₁ H ₂₂ N ₃ , loss of C ₆ H ₇ N, from <i>m/e</i> 409
	317	21	
	407	10	
	408	32	
	409	100	(M + 1) ⁺
	410	28	

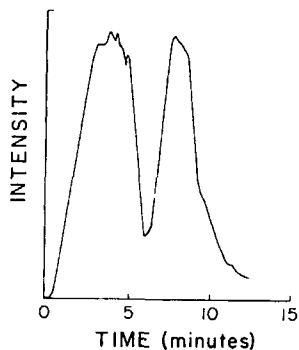
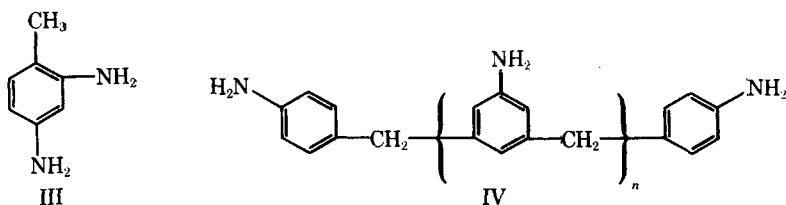


Fig. 2. Intensity vs time for the mass chromatogram of poly-MDI hydrolyzate.

otherwise) yielded amines III and IV, respectively:



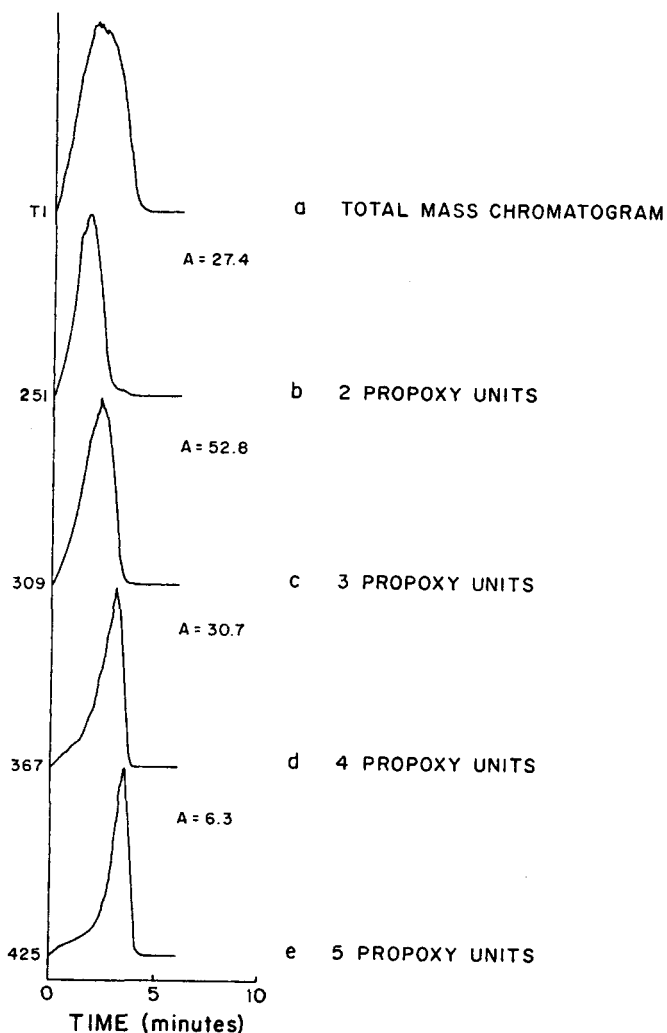


Fig. 3. Intensity vs time for (a) the mass chromatogram of polyol A and (b)–(e) specific ion plots of m/e values of polyol units containing 2 to 5 propoxylations.

Four polyols were used as supplied without further preparation: polyol A, a propoxylated trimethylolpropane (TP-340, Wyandotte); polyol B, a propoxylated 2-(2-aminoethylamino)ethanol (RA-800, Dow); polyol C, a propoxylated sucrose–glycerine (Poly-G 531S, Olin); and polyol D, a propoxylated sucrose–diethanolamine (Poly-G 530SA, Olin).

Polyurethane Foams

Two rigid urethane foams, samples 1 and 2, were prepared in our laboratory by the “one shot” process with an isocyanate index of 1.05. Foam samples 3 and 4 were produced on full-scale processing equipment by the Olin Corporation. The formulations of all four foam samples are listed in Table I.

TABLE IV
The Methane CI Spectrum of a Propoxylated Trimethylolpropane (Polyol A)

<i>m/e</i>	Relative intensity	Tentative assignment
87	9	
99	21	<i>m/e</i> 135 - 2H ₂ O
117	15	<i>m/e</i> 135 - H ₂ O
135	d ^a	(<i>M</i> + 1) ⁺ , 0 propoxy units
143	10	
157	22	<i>m/e</i> 193 - 2H ₂ O
175	17	<i>m/e</i> 193 - H ₂ O
193	d	(<i>M</i> + 1) ⁺ , 1 propoxy unit
215	11	<i>m/e</i> 251 - 2H ₂ O
233	19	<i>m/e</i> 251 - H ₂ O
251	30	(<i>M</i> + 1) ⁺ , 2 propoxy units
291	12	<i>m/e</i> 309 - H ₂ O
309	100	(<i>M</i> + 1) ⁺ , 3 propoxy units
310		
332	5	
337	6	(<i>M</i> + 29) ⁺ , 3 propoxy units
349	10	<i>m/e</i> 367 - H ₂ O
367	65	(<i>M</i> + 1) ⁺ , 4 propoxy units
407	d	<i>m/e</i> 425 - H ₂ O
425	13	(<i>M</i> + 1) ⁺ , 5 propoxy units
483	3	(<i>M</i> + 1) ⁺ , 6 propoxy units
541	d	(<i>M</i> + 1) ⁺ , 7 propoxy units
599	d	(<i>M</i> + 1) ⁺ , 8 propoxy units

^a d = Detectable in spectrum, but intensity was less than 1%.

TABLE V
The Methane CI Spectrum of a Propoxylated 2-(2-Aminoethylamino)ethanol (Polyol B)

<i>m/e</i>	Relative intensity	Tentative assignment
221	d ^a	(<i>M</i> + 1) ⁺ , 2 propoxy units
261	17	<i>m/e</i> 279 - H ₂ O
277	12	
279	100	(<i>M</i> + 1) ⁺ , 3 propoxy units
280	15	
307	17	(<i>M</i> + 29) ⁺ , 3 propoxy units
319	d	<i>m/e</i> 337 - H ₂ O
337	6	(<i>M</i> + 1) ⁺ , 4 propoxy units
395	d	(<i>M</i> + 1) ⁺ , 5 propoxy units
453	d	(<i>M</i> + 1) ⁺ , 6 propoxy units
511	d	(<i>M</i> + 1) ⁺ , 7 propoxy units

^a d = Detectable in spectrum, but intensity was less than 1%.

Sample Hydrolysis

Refluxing aqueous potassium hydroxide was used to prepare the foam hydrolysis products. In a typical run, ~50 mg foam was finely ground with 8.5 g potassium hydroxide. The powdered mixture was placed in a 50-ml round-bottom flask equipped with a magnetic stirrer and a reflux condenser. The foam particles rose to the top upon the addition of 9 ml water. The reaction mixture was stirred under refluxing conditions for 3.5 hr in an oil bath maintained at

TABLE VI
The Methane CI Spectrum of a Propoxylated Sucrose Glycerine (Polyol C)

<i>m/e</i>	Relative intensity	Tentative assignment
75	19	<i>m/e</i> 93 - H ₂ O
77	d ^a	(<i>M</i> + 1) ⁺ of PG ^b
87	12	
99	5	<i>m/e</i> 135 - 2H ₂ O
101	13	
113	11	
115	71	<i>m/e</i> 151 - 2H ₂ O
117	23	<i>m/e</i> 135 - H ₂ O
133	45	<i>m/e</i> 151 - H ₂ O
135	3	(<i>M</i> + 1) ⁺ , PG with 1 propoxy unit
143	3	
151	2	(<i>M</i> + 1) ⁺ , G ^c with 1 propoxy unit
155	3	<i>m/e</i> 209 - 3H ₂ O
167	19	
173	37	<i>m/e</i> 209 - 2H ₂ O
175	3	<i>m/e</i> 193 - H ₂ O
185	10	
191	47	<i>m/e</i> 209 - H ₂ O
193	d	(<i>M</i> + 1) ⁺ , PG with 2 propoxy units
201	9	
209	20	(<i>M</i> + 1) ⁺ , PG with 2 propoxy units
233	d	<i>m/e</i> 251 - H ₂ O
243	25	
249	28	<i>m/e</i> 267 - H ₂ O
251	d	(<i>M</i> + 1) ⁺ , PG with 3 propoxy units
267	99	(<i>M</i> + 1) ⁺ , G with 3 propoxy units
268	13	
295	2	(<i>M</i> + 29) ⁺ , G with 3 propoxy units
301	19	
302	2	
307	20	<i>m/e</i> 325 - H ₂ O
309	d	(<i>M</i> + 1) ⁺ , PG with 4 propoxy units
319	7	
325	100	(<i>M</i> + 1) ⁺ , G with 4 propoxy units
326	17	
349	d	<i>m/e</i> 367 - H ₂ O
353	6	(<i>M</i> + 29) ⁺ , G with 4 propoxy units
359	2	
365	8	<i>m/e</i> 383 - H ₂ O
367	d	(<i>M</i> + 1) ⁺ , PG with 5 propoxy units
383	40	(<i>M</i> + 1) ⁺ , G with 5 propoxy units
384	8	
395	12	
423	2	<i>m/e</i> 441 - H ₂ O
441	10	(<i>M</i> + 1) ⁺ , G with 6 propoxy units
442	2	
453	19	
499	2	(<i>M</i> + 1) ⁺ , G with 7 propoxy units
511	6	
557	d	(<i>M</i> + 1) ⁺ , G with 8 propoxy units
615	d	(<i>M</i> + 1) ⁺ , G with 9 propoxy units

^a d = Detectable in spectrum, but intensity was less than 1%.

^b PG = Propylene glycol.

^c G = Glycerine.

TABLE VII
The Methane CI Spectrum of a Propoxylated Sucrose Diethanolamine (Polyol D)

<i>m/e</i>	Relative intensity	Tentative assignment
75	11	
87	22	
99	11	<i>m/e</i> 135 - 2H ₂ O
101	8	
117	47	<i>m/e</i> 135 - H ₂ O
135	16	(<i>M</i> + 1) ⁺ , PG ^b with 1 propoxy unit
143	20	
164	7	(<i>M</i> + 1) ⁺ , 1 propoxy unit
167	20	
175	3	<i>m/e</i> 193 - H ₂ O
193	7	(<i>M</i> + 1) ⁺ , PG with 2 propoxy units
222	48	(<i>M</i> + 1) ⁺ , 2 propoxy units
243	18	
251	d ^a	(<i>M</i> + 1) ⁺ , PG with 3 propoxy units
262	8	<i>m/e</i> 280 - H ₂ O
280	100	(<i>M</i> + 1) ⁺ , 3 propoxy units
281	14	
291	d	
301	16	
308	d	(<i>M</i> + 29) ⁺ , 3 propoxy units
320	d	<i>m/e</i> 338 - H ₂ O
338	44	(<i>M</i> + 1) ⁺ , 4 propoxy units
366	5	(<i>M</i> + 29) ⁺ , 4 propoxy units
378	5	<i>m/e</i> 396 - H ₂ O
396	11	(<i>M</i> + 1) ⁺ , 5 propoxy units
424	d	(<i>M</i> + 29) ⁺ , 5 propoxy units
454	d	(<i>M</i> + 1) ⁺ , 6 propoxy units
512	d	(<i>M</i> + 1) ⁺ , 7 propoxy units
570	d	(<i>M</i> + 1) ⁺ , 8 propoxy units

^a d = Detectable in spectrum, but intensity was less than 1%.

^b PG = Propylene glycol.

150°C. This hydrolysis process required several additional hours when the foam samples were not finely ground. After the allotted time, 25 ml water was added to the flask and the reaction cooled to room temperature. This resulted in a colorless solution with several brown particles floating on the surface. This solution was extracted with two 20-ml aliquots of dichloromethane, at which point the brown particles dissolved. The combined extracts were dried over 1 g anhydrous magnesium sulfate and then filtered.

A modification of Mulder's¹¹ sealed ampoule method for urethane hydrolysis was employed when the initial sample size was less than 10 mg. The reaction vessel was prepared by sealing one end of a 6-mm-O.D., ~200-mm-long medium-walled glass tube. A 5-mg foam sample and 250 mg water were added to the tube, and after one freeze-pump-thaw cycle the tube was sealed under vacuum. Several reaction tubes that were prepared in this fashion were placed in a stainless-steel bomb that contained water for pressure equilization. The samples were heated for 1 hr at 250°C. After cooling the bomb to room temperature, the glass ampoules were emptied and rinsed thoroughly with 1 ml methanol. The samples were evaporated to dryness with a stream of nitrogen,

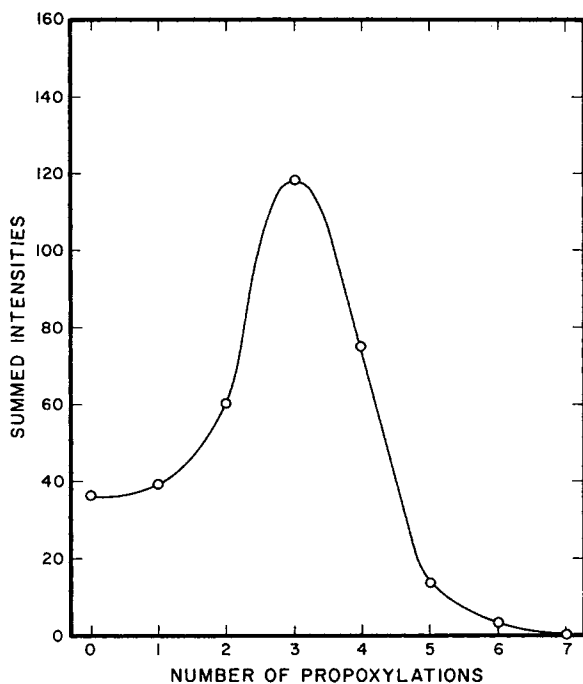


Fig. 4. Molecular weight distribution of polyol A.

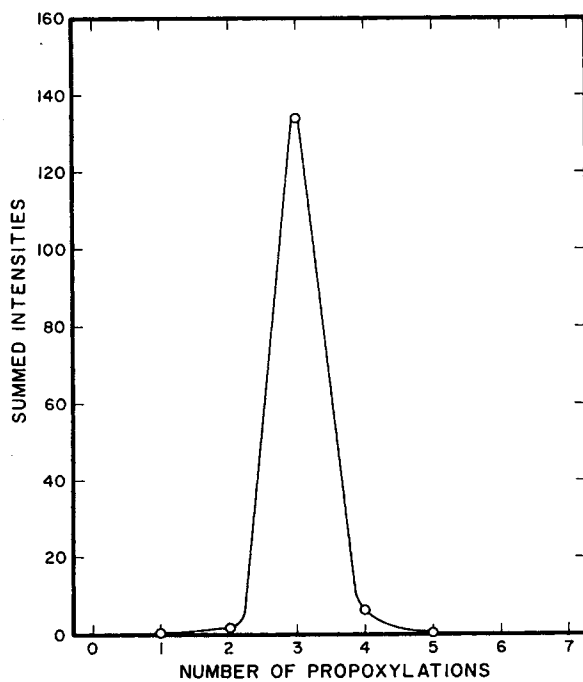


Fig. 5. Molecular weight distribution of polyol B.

redissolved in methanol, and filtered to remove insoluble silicates. No further preparation of the samples was necessary.

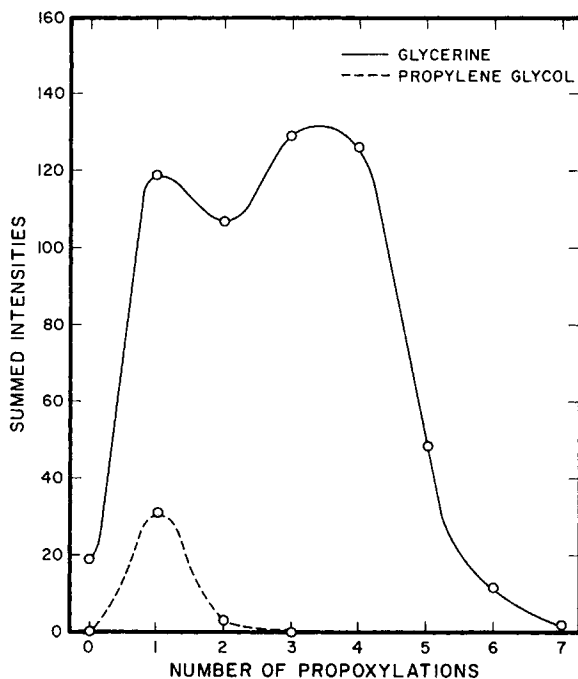


Fig. 6. Molecular weight distribution of polyol C: (—) glycerine; (---) propylene glycol.

Mass-Spectrometric Analysis

Both EI and chemical ionization mass spectra were obtained using a Hewlett-Packard Model 5982 GC-MS system equipped with a Model 5933A data system. Samples (ca. 10 μg) were introduced into the ion source (150°C) via a direct insertion probe that was slowly heated from ambient to 325°C over a period of 10 min. Mass spectra between m/e 60 and 700 were recorded and stored every 8 sec. The CI-MS experiments used methane (0.5 torr, UGP grade) bled into the ion source coaxially to the direct insertion probe.

Liquid Chromatography

Separation of the polyamines was carried out on a Perkin-Elmer Model 601 liquid chromatograph equipped with a Model LC-55 variable wavelength detector operating at 240 nm. A 25-cm silica column (Sil-X-I, Perkin-Elmer Corporation) was used isocratically with an isopropanol: hexane mobile-phase mixture (30:70 ratio) at a temperature of 30°C.

RESULTS AND DISCUSSION

Analysis of Standards

Amine Derivatives of Isocyanates

The hydrolyzate from TDI was heated on the direct insertion probe at 30°C/min from 25° to 300°C. The CI-MS spectrum shown in Table II contains five ions, and tentative assignments are listed for each. Methane chemical

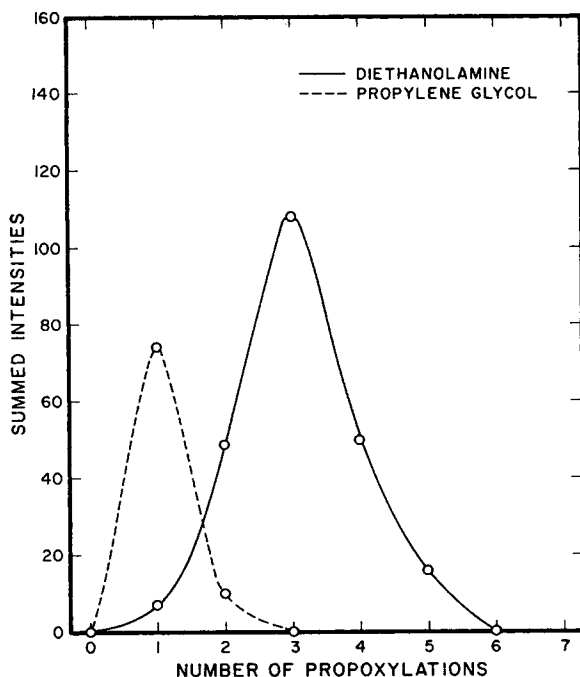


Fig. 7. Molecular weight distribution of polyol D: (—) diethanolamine; (---) propylene glycol.

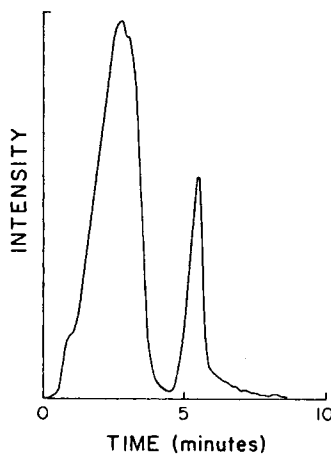


Fig. 8. Total ion reconstruct of CI-MS of hydrolysis of foam I.

ionization spectra are characterized by ion-molecule adducts which appear at $(M + 1)^+$, $(M + 29)^+$, and $(M + 41)^+$, where M is the mass of the sample molecule.¹² CI spectra often contain few fragment ions, and the $(M + 1)^+$, $(M + 29)^+$, and $(M + 41)^+$ adducts can be identified because they appear in relative intensities of approximately 10:3:1, respectively. The mass spectrum in Table II contains ions at m/e 123, 151, and 163 with relative intensities of 10:3:0.5, thus the molecular weight of the compound is most likely 122 amu. This mass spectrum also contains an M^+ ion, which is the product of a charge transfer re-

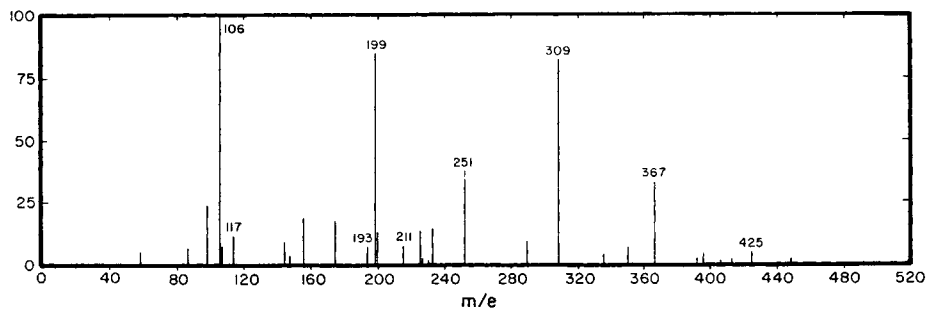


Fig. 9. Spectrum of first peak of Figure 8.

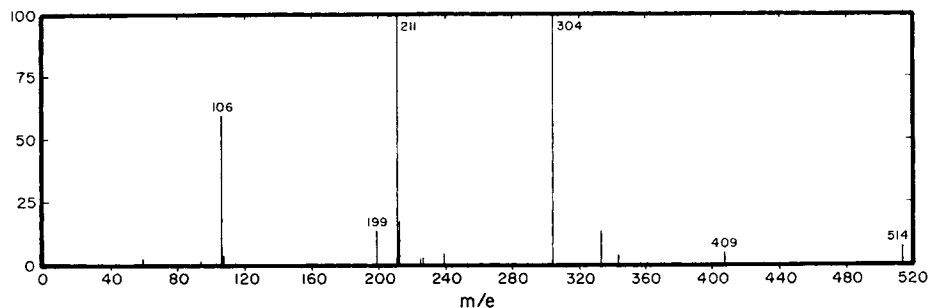


Fig. 10. Spectrum of second peak of Figure 8.

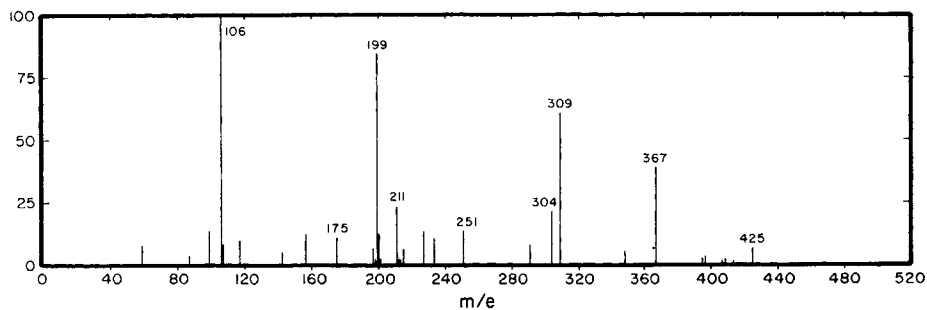


Fig. 11. Summed methane CI spectrum of sample foam 1.

action.¹³ A combination of the M^+ , $(M + 1)^+$, $(M + 29)^+$, and $(M + 41)^+$ ions is characteristic of the methane CI spectra of simple amines.¹⁴

The homologs of poly-MDI were separated prior to CI-MS analysis by high-pressure liquid chromatography (HPLC). As shown in Figure 1, four compounds were detected in polymer IV. These compounds were identified by CI-MS and retention time comparisons with authentic samples as (1) solvent, (2) ortho, $n = 0$, (3) para, $n = 0$, (4) $n = 1$, and (5) $n = 2$. Table III contains the CI spectra of peaks 2 through 5. The ortho and para isomers of IV ($n = 0$) produced nearly identical spectra containing M^+ , $(M + 1)^+$, $(M + 29)^+$, and $(M + 41)^+$ adduct ions. Unlike TDI, both isomers produced a fragment ion at m/e 106, and it has been tentatively assigned to the loss of C_6H_7N which is formed by cleavage of the bond between the methylene carbon and the aromatic ring in the $(M + 1)^+$ adduct. The mass spectrum of IV ($n = 1$) shows the loss of C_6H_7N (m/e 211)

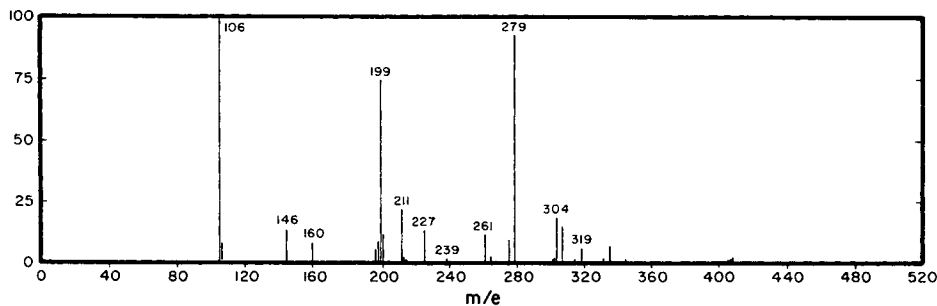


Fig. 12. Summed methane CI spectrum of sample foam 2.

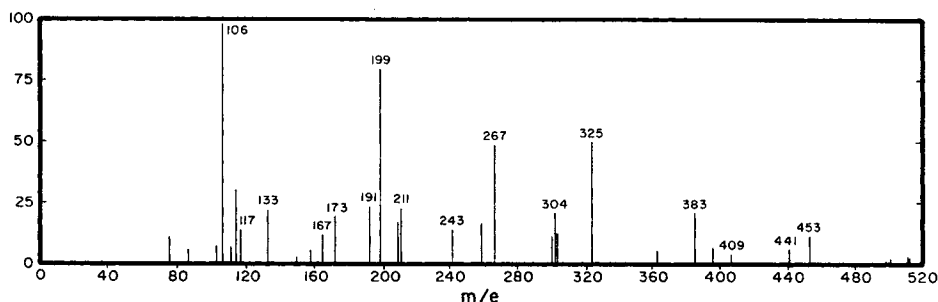


Fig. 13. Summed methane CI spectrum of sample foam 3.

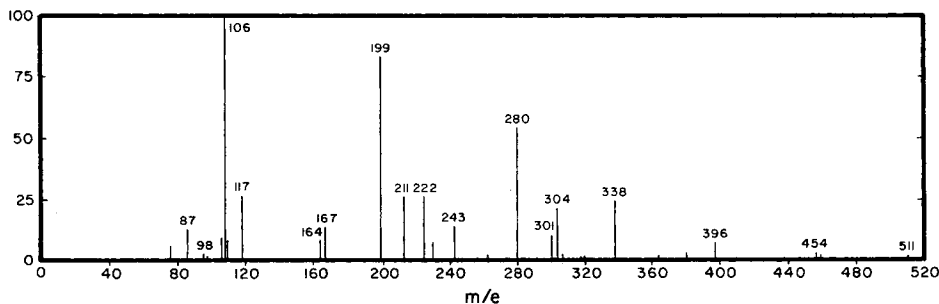


Fig. 14. Summed methane CI spectrum of sample foam 4.

from m/e 304 and a fragment ion at m/e 106, assigned as $C_6H_8N^+$. The CI spectrum of IV ($n = 2$) contains fragment ions at m/e 106 and 211 and the loss of C_6H_7N from $(M + 1)^+$ to form m/e 316.

The objective of these experiments was to develop a rapid method for the identification of hydrolyzates from isocyanates in urethane foams. The process of separating the homologs of IV by HPLC, followed by CI-MS analysis, proved to be an accurate but time-consuming procedure. To simplify and shorten the time for analysis, the hydrolyzate mixture of the isocyanate standards was placed in the direct insertion probe and the sample was heated at $30^\circ C/min$ from 25° to $325^\circ C$. During the heating period, the mass spectrum from m/e 60 to 700 was continually recorded. Figure 2 represents the mass chromatogram (the summed intensity of all ions between m/e 60 and 700) from a sample of poly-MDI hydrolyzate. By comparing the sequential mass spectra that were recorded during

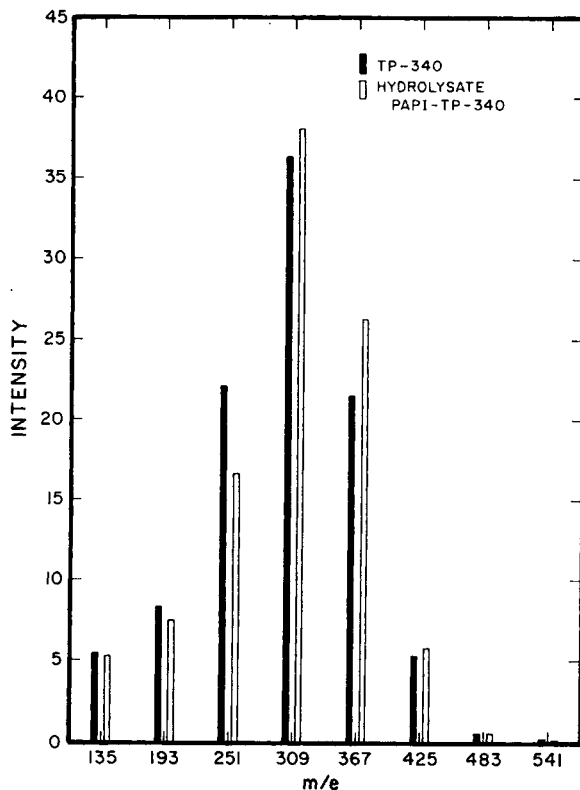


Fig. 15. Propoxylated trimethylolpropane.

this experiment with standard spectra in Table III, we identified three amine components in poly-MDI. Compound IV ($n = 0$) volatilized at the lowest temperature and it was the only compound detected in the first peak. The second peak contained mostly IV ($n = 1$), and IV ($n = 2$) was detected in low concentrations in the following edge. The tail of the second peak also contained ions of very low intensity at m/e 514 and 619. These m/e values correspond to the appropriate masses of the $(M + 1)^+$ adducts of IV ($n = 3$) and IV ($n = 4$). The intensity of these two ions was extremely low, and the $(M + 29)$ and $(M + 41)^+$ adducts, if present, were below the lower detection limit of the instrument. Thus the data suggest that the $n = 3$ and $n = 4$ homologs of IV were present in very low concentrations.

Polyol Fraction

Standard polyols were analyzed by CI-MS without any prior sample preparation by heating at $30^\circ\text{C}/\text{min}$ from 25° to 325°C in the direct insertion probe. The mass chromatograms of all the polyols in this study contained a single broad peak such as the one shown in Figure 3(a). Figures 3(b) through 3(e) are single ion plots of the major m/e values in the spectrum of this polyol. The intensity of m/e 251 ion maximized at a shorter time than the mass chromatogram, Figure 3(a), and higher m/e values reached maximum intensities at progressively longer times. These data are direct evidence that lower molecular weight compounds

evaporated from the solids probe at lower temperatures than did higher molecular weight species.

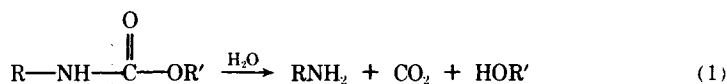
The tabulated methane CI spectra and tentative assignments for polyols A, B, C, and D appear in Tables IV through VII, respectively. The intensities of all ions were averaged throughout the entire mass chromatogram to minimize errors from compound volatility. The CI spectra of all four polyols were similar in that each contained $(M + 1)^+$ and $(M + 29)^+$ adducts and fragment ion corresponding to losses of one, two, or three water molecules $[(M + 1) - n\text{H}_2\text{O}]^+$, $n = 1, 2, \text{ or } 3$. Polyfunctional alcohols have been reported to form $(M + 1)^+$ and $(M + 29)^+$ adducts under methane CI conditions and readily lose one or more water molecules.^{15,16}

The most distinctive feature of these CI spectra is that each individual polyol can be distinguished from other propoxylated homologs. Each compound differs from the next member of the series by one propoxy group (58 amu). For example, the $(M + 1)^+$ ions from the derivatives of trimethylolpropane were observed at m/e 135, 193, 251, 309, 367, 425, 483, 541, and 599, corresponding to the presence of zero to eight propoxylations. By summing all adduct and fragment ions formed from each polyol, the relative amount of each homolog can be approximated from the CI spectrum. The molecular weight distribution of polyol A, shown in Figure 4, was determined by summing the intensities of $(M + 29)^+$, $(M + 1)^+$, and $[(M + 1) - n\text{H}_2\text{O}]^+$ species for each propoxylated compound. Polyol A consisted primarily of compounds containing two, three, and four propoxylations, but species containing zero, one, and five propoxy groups were also present.

Similar plots of summed ion intensity versus number of propoxylations are shown in Figures 5–7 for polyols B, C, and D. Polyol B contained homologs with three and four propoxylations in a ratio of 13:1 and compounds with five, six, and seven propoxy groups were detected in low concentrations. Polyol C consisted of homologs with a wider molecular weight range (zero to six propoxylations), but one through four propoxy groups per compound were predominant. The CI spectrum also contains ions of the appropriate masses to represent a propylene glycol with the addition of one propoxy group. These ions were of low intensity and are assumed to originate from an impurity in polyol C, which was of commercial grade. Polyol D contained three major polyol homologs with three, four, and five propoxy groups. Ions corresponding to zero, one, or two propoxy groups were not detected, but homologs with six to eight propoxylations were identified from the CI spectrum. Ions characteristic of a propoxylated propylene glycol were present in low abundance.

Foam Hydrolyzates

Several methods for hydrolyzing polyurethane foam samples have appeared in recent literature.^{10,11} Under base-catalyzed conditions, ester and amide bonds are hydrolyzed while either linkages remain intact.¹⁰ Hydrolysis of a rigid polyurethane produces a mixture containing a polyol and a polyamine derivative of the original isocyanate, Eq. (1). Our first series of experiments were used to evaluate the extent



of the reaction shown in eq. (1) and to observe if there was any further degradation of the polyamines or the polyols.

The two procedures for sample workup, the sealed tube hydrolysis, and the refluxing base methods, were applied to sample foams 1 and 4 to evaluate the extent of hydrolysis and the ease of sample workup necessary for CI-MS analysis for both procedures. The extent of sample hydrolysis was judged by the intensity of the ions in the mass spectrum of the foam hydrolyzate that were attributable to the polyamine and the polyol fractions. The presence of additional ions which could complicate spectral interpretations was also considered. The ease of sample workup was judged upon how much time was required to prepare the hydrolysate for CI-MS analysis. The CI spectra of the two urethane foam hydrolyzates prepared by the two procedures were found to be equal in intensity and free of interfering ions. However, the hydrolyzate from the sealed tube method was more difficult to prepare for analysis because it formed an insoluble brown residue of unknown composition. To avoid any complications from incomplete hydrolysis or degradation of the polyamine or polyol fractions, the sealed tube method was not pursued further. The refluxing base hydrolysis was chosen for all sample preparations reported herein.

The four polyurethane foam hydrolyzates yielded similarly shaped mass chromatograms containing two peaks, and the trace shown in Figure 8 for sample foam 1 was representative of the relative intensities observed. The CI spectrum recorded at the top of the first peak is shown in Figure 9. The intense ions at m/e 106, 199, and 227 were readily identified as polyamine IV with $n = 0$, and m/e 251, 309, 367, and 425 are characteristic of polyol A. The spectrum recorded at the top of the second peak, shown in Figure 10, contains ions of prominent intensities at m/e 106, 211, 304, 409, and 514. These ions and their relative intensities match those from polyamine IV, $n = 1$, with small contributions from compounds of $n = 2$ and 3. The second peak did not contain ions representative of the polyol.

The CI spectra of the hydrolyzed sample, shown in Figure 11, were averaged over the entire mass chromatogram. This spectrum contains all the ions that are characteristic of a mixture of polyol A and the amine from poly-MDI in a 3:5 ratio.

The composite mass spectra from sample foams 2, 3, and 4 are shown in Figures 12-14, respectively. These spectra are free of prominent interfering ions and were used without difficulty to identify the polyol and polyamine fractions. The CI spectra of sample foams 3 and 4 contained ions at m/e 99 and 117, which are most likely from propylene glycol. This observation was not surprising since the standard polyol samples C and D, which were obtained from the same manufacturer, also contained propylene glycol in low concentrations.

The freedom of interfering ions in the spectra of the hydrolyzates indicated that there was little polyol or polyamine degradation in sample preparation. Aromatic amides are known to be stable and very chemically resistant to decomposition in base. However, there was still some question as to whether the recovered polyol was representative of the original polyol. Figure 15 compares the CI-MS-determined molecular weight distributions from recovered and unreacted samples of polyol A. There is a slight difference in the relative abundances of the 2- and 4-propoxylated compounds, but the other homologs agree in intensity to within experimental error. Thus, the hydrolysis and workup procedure appears to be satisfactory.

CONCLUSIONS

Samples of polyurethane foam that were hydrolyzed by the refluxing base method were sufficiently free of degradation products that the component parts of the formulation could be identified by CI-MS techniques. The mass spectra of the hydrolysis products from rigid urethane foams were predictable for homologous series of polyols and polyamines that were studied. The molecular weight distribution of the polyamine fraction and the relative concentrations of the homologs in the polyol were determined from the CI spectrum and HPLC data from each material. The CI-MS procedure is sensitive to trace concentrations and thus can be used to identify impurities in the polyol and isocyanate components used in foam manufacture.

References

1. F. D. Hileman, K. J. Voorhees, L. H. Wojcik, M. M. Birky, P. W. Ryan, and I. N. Einhorn, *J. Polym. Sci.*, **13**, 571 (1975).
2. W. H. T. Davison, and P. J. Corrish, *J. Chem. Soc.*, 2428 (1955).
3. D. J. David, and H. B. Staley, *Analytical Chemistry of the Polyurethanes*, Wiley-Interscience, New York, 1969.
4. O. Kinoshita, *Shikizai Kyokaishi*, **44**, 273 (1971).
5. J. E. Sheridan, and C. A. Haines, *J. Cell. Plast.*, **7**, 135 (1971).
6. P. E. Slade and I. T. Jenkins, *J. Polym. Soc. C*, **6**, 27 (1964).
7. I. N. Einhorn, M. S. Ramakrishnan, and R. W. Mickelson, *J. Appl. Polym. Sci.*, **00**, 000 (0000).
8. M. B. Jackson and D. H. Soloman, *Anal. Chem.*, **44**, 1074 (1972).
9. I. LiGotti, R. Piacentini, and G. Bonomi, *Mater. Plast. Elastomeri*, **36**, 213 (1970).
10. B. Dawson, S. Hopkins, and P. R. Sewell, *J. Appl. Polym. Sci.*, **14**, 45 (1970).
11. J. I. Mulder, *Anal. Chim. Acta*, **38**, 563 (1967).
12. F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).
13. S. Zitrin, and J. Yinon, *Org. Mass Spectrosc.*, **11**, 388 (1976).
14. M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).
15. A. M. Hogg and T. L. Wagabhushan, *Tetrahedron Lett.*, **47**, 4827 (1972).
16. M. S. B. Munson, *Anal. Chem.*, **43**, 28A (1971).

Received May 17, 1977