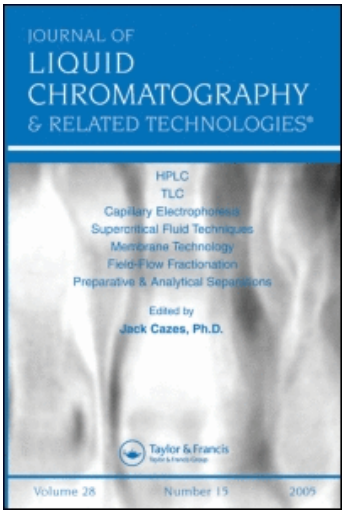

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Characterization of New Isocyanate Adducts by High Performance Size Exclusion Chromatography

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CHARACTERIZATION OF NEW ISOCYANATE ADDUCTS BY HIGH PERFORMANCE SIZE EXCLUSION CHROMATOGRAPHY

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ABSTRACT

The low molecular weight reaction products ("adducts") of m-tetramethylenexylene diisocyanate (m-TMXDI) and trimethylol propane (TMP) are characterized by high performance size exclusion chromatography using a state-of-the-art automated computer system. The separations of several m-TMXDI/TMP adducts on different column and solvent systems demonstrate excellent resolution and provide quantitative estimates of the product distributions. With proper assignment of molecular weight to well-resolved peaks, both number-average molecular weights and wt% isocyanate content can be determined from area measurements, in excellent agreement with measurements by vapor pressure osmometry.

INTRODUCTION

Polyurethanes are an established class of polymers used in various applications such as elastomers, coatings resins, and flexible and rigid foams[1-3]. More recently, polyurethanes

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derived from aliphatic diisocyanates are attracting interest primarily due to their durability, particularly with regard to light stability[4]. Two new aliphatic isocyanates[5] have recently become available to the polyurethane industry, namely 1,3-bis(1-isocyanato-1-methylethyl)benzene and 1,4-bis(1-isocyanato-1-methylethyl)benzene. They are also known commercially as m-TMXDI (m-tetramethylenexylene diisocyanate) and p-TMXDI (p-tetramethylenexylene diisocyanate).

It is well known that size exclusion chromatography (SEC) provides a rapid and precise technique for determining the molecular weight (MW) and molecular weight distributions (MWDs) of polymers, provided calibration standards are available. In recent years, the development of 10μm and now 5μm particle size substrates has significantly enhanced the speed and resolution of SEC to the "high performance" (HPSEC) level.[6] In particular, this improved resolution has been extremely useful for the separation and quantitation of low molecular weight mixtures[6-8] soluble in commonly-used organic solvents. It is estimated that as much as 50% of the HPSEC analyses performed in this laboratory fall into this low (<5,000 g/mole) MW region.

The present study is a HPSEC investigation of the reaction products (or simply "adducts") of m-TMXDI and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (trimethylol propane or TMP). The structural formulas of these reactant materials are shown in Figure 1. Also shown is the product formed by the reaction of three moles of m-TMXDI and one mole of TMP, the "3/1" species. Since excess m-TMXDI is actually used in the reaction, other possible by-products of this reaction are the 1/1, 2/1, 5/2, 7/3 and even higher molecular weight adducts, shown schematically in Figure 2.

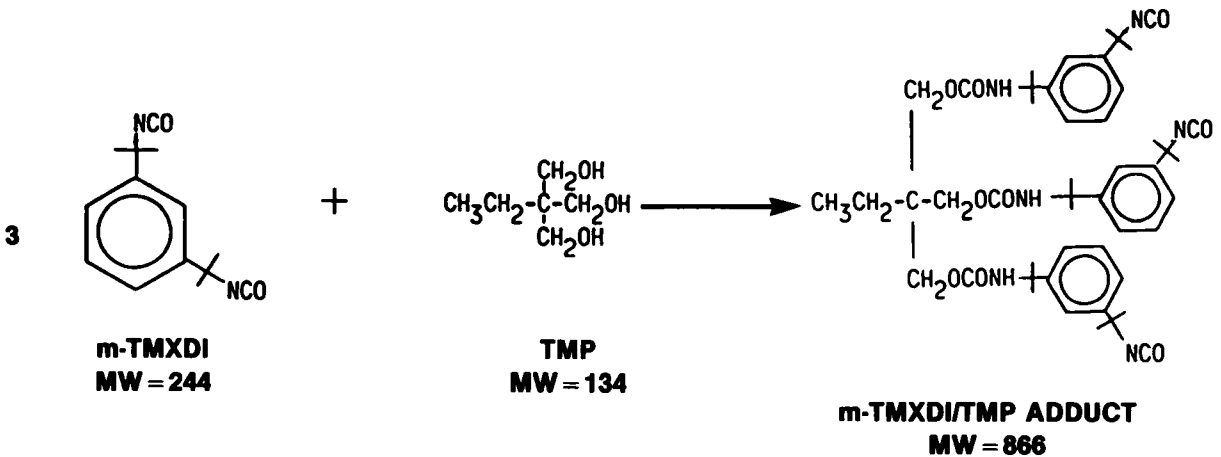


Figure 1: Reaction of m-TMXDI and TMP.

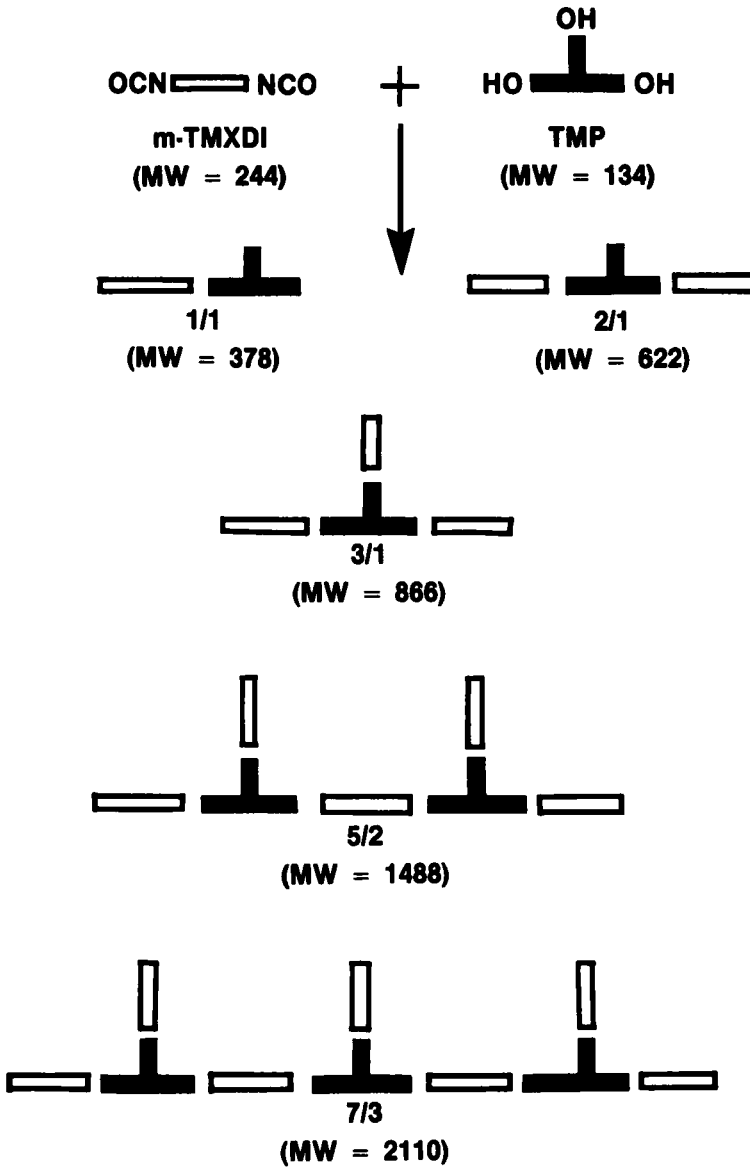


Figure 2: m-TMXDI/TMP Adducts.

It will be demonstrated that high performance size exclusion chromatography is a rapid, precise and accurate technique for characterizing the product distribution of this reaction.

MATERIALS

Four adduct preparations were used in this study. Two typical samples (S-78 and S-118) contain a high proportion (55-65 area %) of the desired 3/1 species. The two other samples (S-80 and S-116) were selected from a statistically designed experiment to demonstrate the resolution and scope of the HPSEC columns used. These latter samples are not typical preparations and contain only <25 area % of the 3/1 adduct species.

EXPERIMENTAL

Two Waters Associates Model 150C liquid chromatographs with two different solvents were used in this study. All samples were run at 0.3 % (w/v) with an injection volume of 200 µL and a flow rate set at 1.0 mL/min. To monitor flow rate changes, sulfur[9] was used as an internal standard at ~0.03 % (w/v). The major portion of this study was done using methylene chloride (HPLC Grade, BAKER ANALYZED®) as solvent. The other instrument utilized reagent grade tetrahydrofuran (THF, BAKER ANALYZED®) as the mobile phase.

All samples were chromatographed on three column sets in the two solvents. The column dimensions are all nominally 30 cm in length with 8 mm ID; they are packed with styrene-divinylbenzene gel. In methylene chloride, a four-column set of ULTRAGEL® MXL's (Analytical Sciences, Inc. (ASI), Santa Clara, CA) was used. These mixed pore-size columns have 10 µm gel particles with plate counts rated at greater than 30,000 plates/meter. A second four-column bank consisted of PLgel® (Polymer

Laboratories, Amherst, MA) was also used with methylene chloride solvent. These columns have efficiencies greater than 50,000 plates/meter resulting from the 5 μm particle size packing. The column porosities of the PLgel® set are 1000, 500, 100, and 50Å. For the THF system, the 6 μSTYRAGEL® columns consist of various porosities ($1\text{-}10^4$ Å, 2-500Å and 3-100Å) with a plate count of around 10,000 plates/meter. These 10μm particle size columns have been in use for over 6 years.

All chromatography data were collected and analyzed on a Hewlett packard (HP) Laboratory Automation System (LAS-3357) with a rate of data transfer equal to 0.5 Hz. Calculations of molecular weight distributions were performed with software obtained originally from HP, but modified extensively to fit our needs over the past six years.

Number-average molecular weights, $\bar{M}_n$ were determined by vapor pressure osmometry (VPO) using a Wescan Model 233 instrument. The calibration was performed with benzil as the standard in toluene. All samples were run in toluene at four or more concentrations, and the $\bar{M}_n$ values were obtained from conventional plots of $\Delta R/c$ vs c. The data were treated by a linear least squares regression program. These VPO data were obtained about one month after the HPSEC analyses to assure sample integrity.

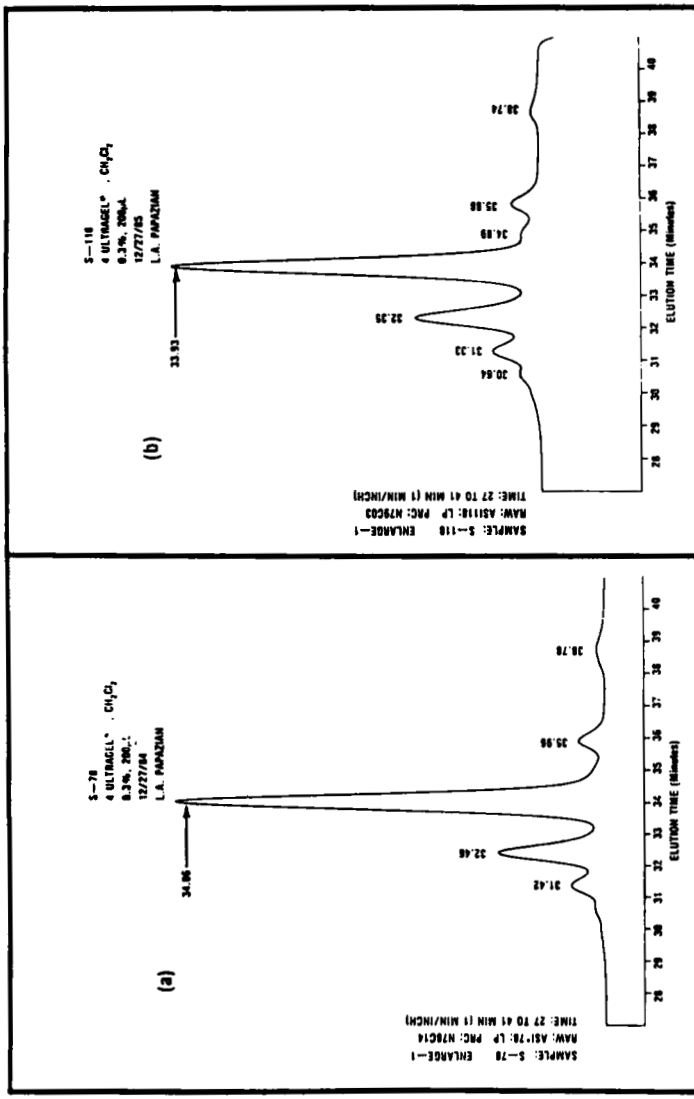
RESULTS AND DISCUSSION

Results obtained with ASI ULTRAGEL® columns in methylene chloride are given in Figure 3. (In all chromatograms, solvent-related and internal standard peaks are not shown.) For samples S-78 and S-118, the largest peak is assumed to be the 3/1 isocyanate/polyol adduct, MW = 866 g/mole; other peaks at lower elution times are most likely the 5/2 and 7/3 adducts, MW = 1488 and 2110 g/mole, respectively. The presence of the 2/1 adduct at

almost 34 minutes elution time is detectable in the S-118 sample chromatogram (Figure 3(b)) but not for the S-78 adduct sample. The peak eluting at around 39 minutes has been shown to be m-TMXDI remaining after a stripping process. More complex product distributions are found for the S-116 and S-80 adduct samples having a higher proportion of unresolved higher molecular weight (i.e., molecular size) species; as a result, the assignment of molecular weights to all peaks becomes much more difficult.

When these four samples are analyzed with PLgel® columns in methylene chloride, one obtains the chromatograms illustrated in Figure 4. The greater resolving power of these 5μm columns is particularly evident in the chromatogram of sample S-78 (Figure 4(a)). One now finds a well-resolved peak for the 2/1 species at ~30.7 minutes (this peak is not evident in Figure 3(a)). The possibility of sample and/or column changes was checked by running these samples again with the ULTRAGEL® columns; no differences from the original chromatograms were found.

In tetrahydrofuran with μSTYRAGEL® columns, similar product distributions were found for the typical (S-78 and S-118) adduct preparations, as shown in Figures 5(a) and 5(b). For these type materials, very little work has been done in THF due to the possibility of water absorption in this polar solvent and its reaction with free isocyanate groups. It is interesting, however, that for these simple preparations, the product distributions are quite similar to those found in methylene chloride. The chromatograms of the other preparations (the S-80 and S-116 adducts) are different, and several new early peaks are evident (Figures 5(c) and 5(d)). These new peaks could possibly be assigned to branched species of higher molecular weight formed by reaction of the isocyanate groups with traces of water in THF.



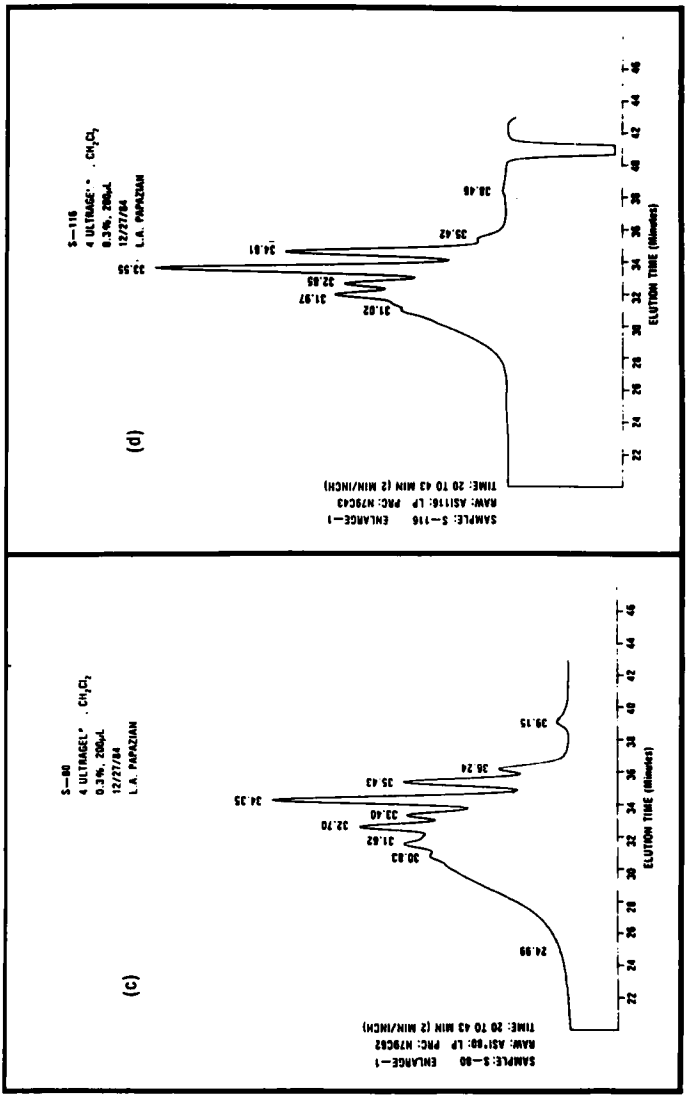
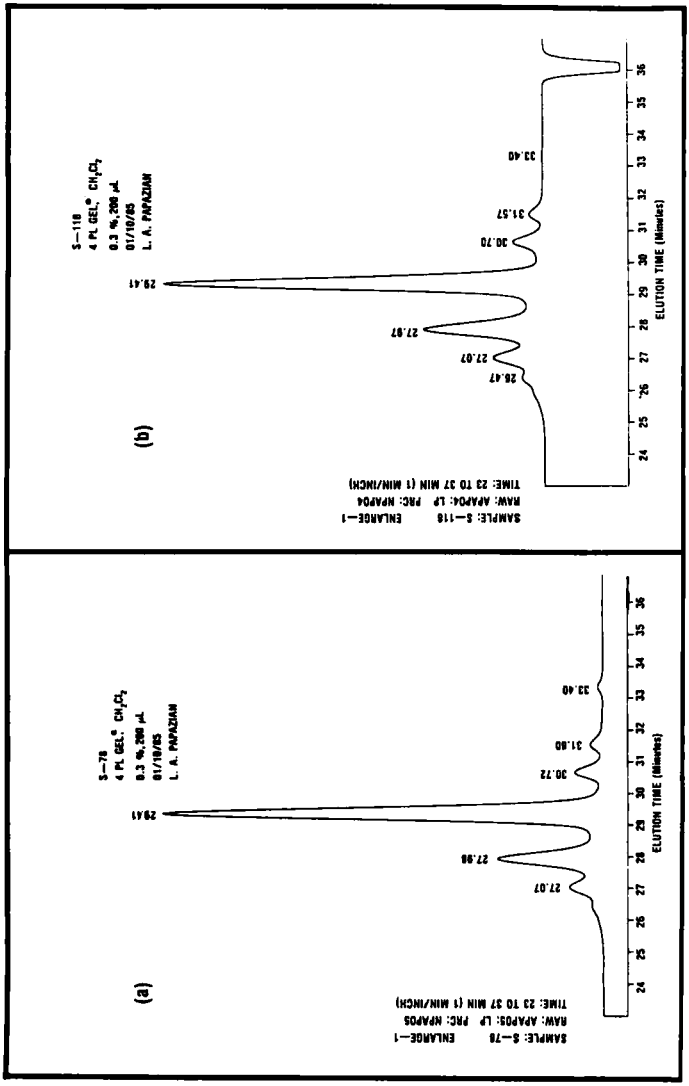


Figure 3: Chromatograms of Adduct Samples obtained with ULTRAGEL® columns in Methylene Chloride: (a) S-78, (b) S-118, (c) S-80, (d) S-116.



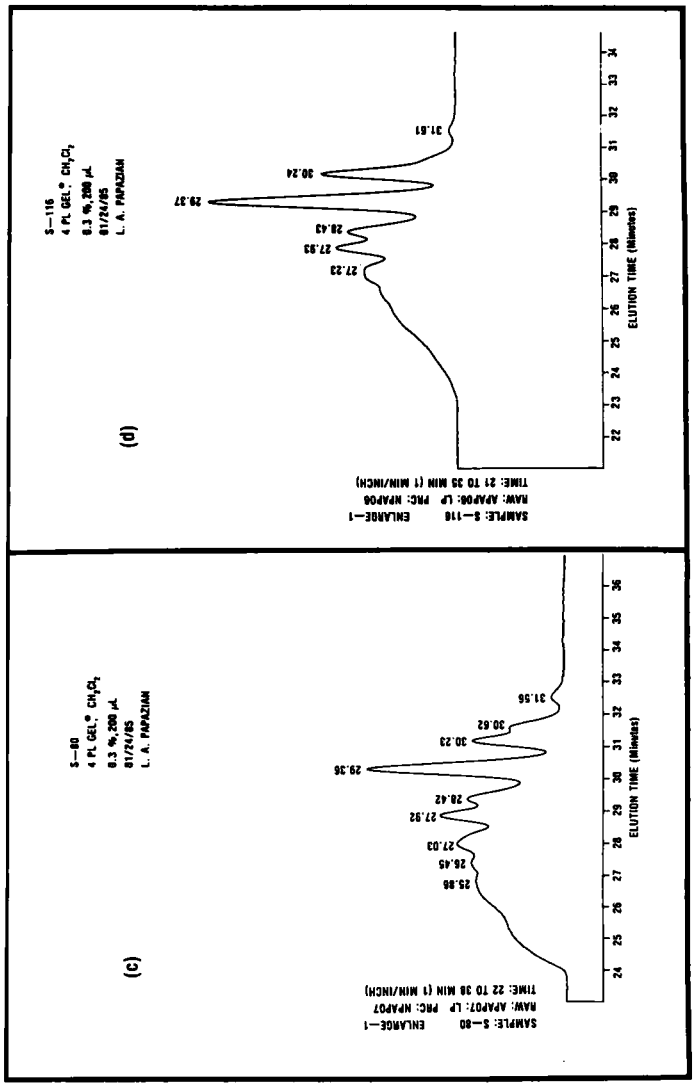
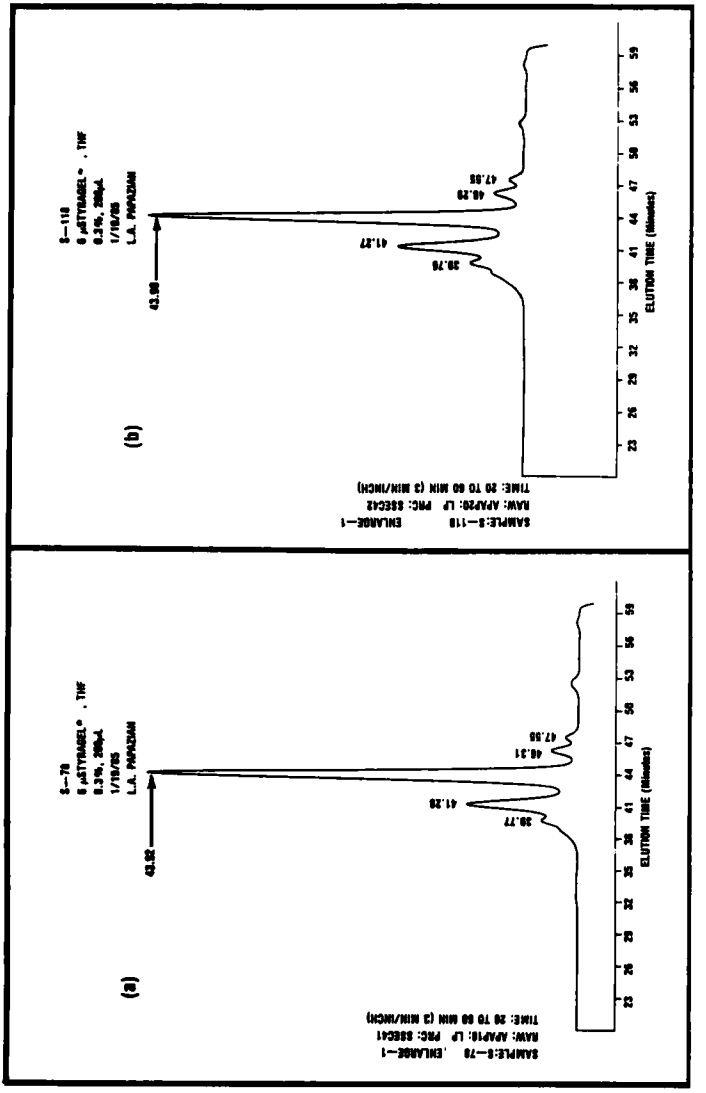


Figure 4: Chromatograms of Adduct Samples obtained with PLgel® columns in Methylene Chloride: (a) S-78, (b) S-118, (c) S-80, (d) S-116.



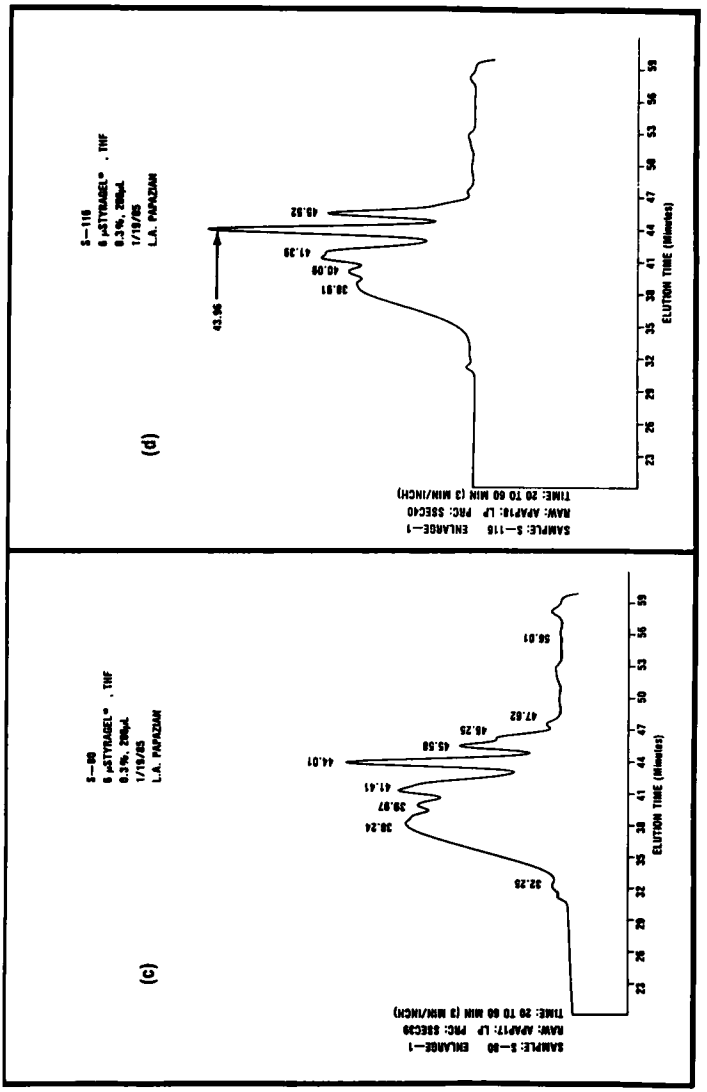


Figure 5: Chromatograms of Adduct Samples obtained with µSTYRAGEL® columns in Tetrahydrofuran: (a) S-78, (b) S-118, (c) S-80, (d) S-116.

By computerized data analysis, the relative area % of each species in each sample may easily be determined. For the 3/1 species, such data are summarized in chronological order in Table 1 along with the analysis date and conditions. For the two "typical" samples (S-78 and S-118) one observes very good stability over a short (1-2 month) time period and about 20% change in 3/1 content over 6 months. This decrease of 3/1 content is reflected in a small increase of larger-sized species (not shown) in the corresponding chromatograms.

An attempt was made to calculate MWDs for these samples, using techniques commonly applied to high MW polymers[10,11]." If

TABLE 1

HPSEC Determination of 3/1 Adduct

Sample	Analysis Date	Column[1] Set	Area % of 3/1 Species
S-78	12/19/84	A	65.9
	1/10/85	B	64.0
	1/19/85	C	64.4
	1/29/85	A	65.4
	3/20/85	B	65.5
	6/25/85	B	51.7
S-118	12/19/85	A	57.5
	1/10/85	B	55.8
	1/19/85	C	54.7
	1/29/85	A	57.5
	6/25/85	B	48.0
S-80	12/21/85	A	17.3
	1/10/85	B	16.4
	1/19/85	C	14.1
	1/29/85	A	15.8
	6/25/85	B	11.0
S-116	11/06/84	A	26.9
	1/10/85	B	22.9
	1/19/85	C	20.7
	1/29/85	A	22.7
	6/25/85	B	14.2

1. Column Set A-ULTRAGEL®; B-PLgel®; C-μSTYRAGEL®

the molecular weights of each peak are known, then every chromatogram provides calibration data in addition to the complete product distribution information (area % of each peak). For each run, the major peak was assumed to be the 3/1 species and other peaks were assigned accordingly (see Figure 2). For the more complex chromatograms of samples S-80 and S-116, the internal standard elution time was utilized to help determine these molecular weight assignments. The molecular weight-elution time data were fitted to a cubic spline regression analysis prior to the computer calculation of the moments of the distribution. For some samples, the cubic spline function gave a better fit than a linear model. This latter model would have been adequate in most cases due to the relatively short elution-time span of these samples. An example of a calibration curve is shown in Figure 6 for sample S-78. Figures 7 and 8 are the differential molecular weight curves for samples S-118 and S-116 along with the moments of the distributions, $\bar{M}_n$ and $\bar{M}_w$. These results are summarized in Table 2.

TABLE 2

Summary of Molecular Weight Data

Technique:	← HPSEC →				Vapor Pressure Osmometry
	$\bar{M}_n$ (g/mole)		$\bar{M}_w$ (g/mole)		$\bar{M}_n$ (g/mole)
Columns:	ASI	PL	ASI	PL	
Sample					
S-78	875	970	1050	1110	1010
S-118	954	1000	1180	1220	1080
S-116	1290	1210	1680	1980	1500
S-80	1300	1420	2840	2320	1680

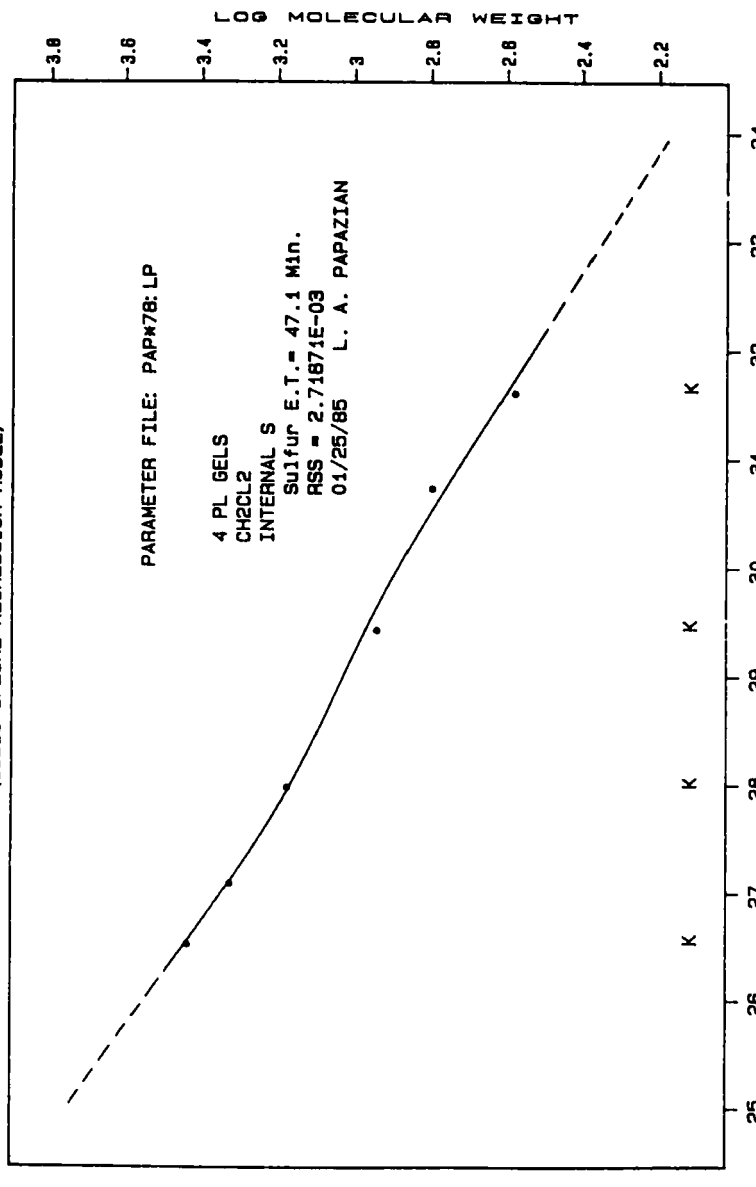


Figure 6: HPSEC Calibration Plot for sample S-78.

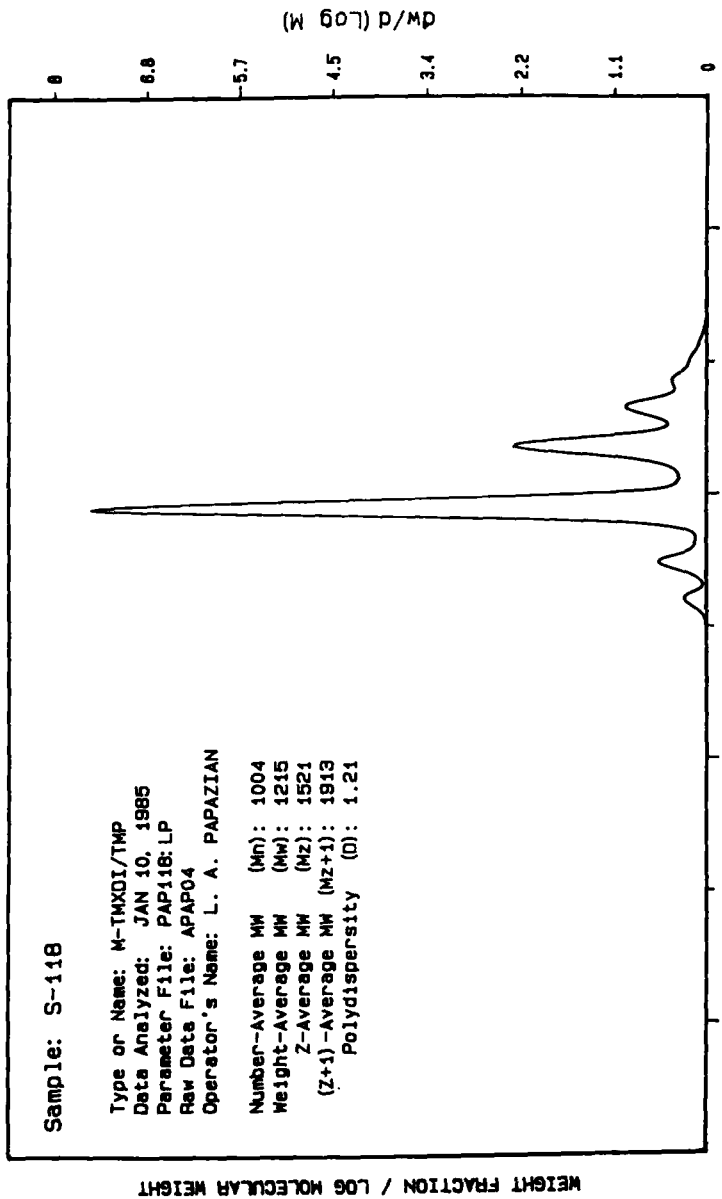


Figure 7: Differential Molecular Weight Distribution Curve for Sample S-118.

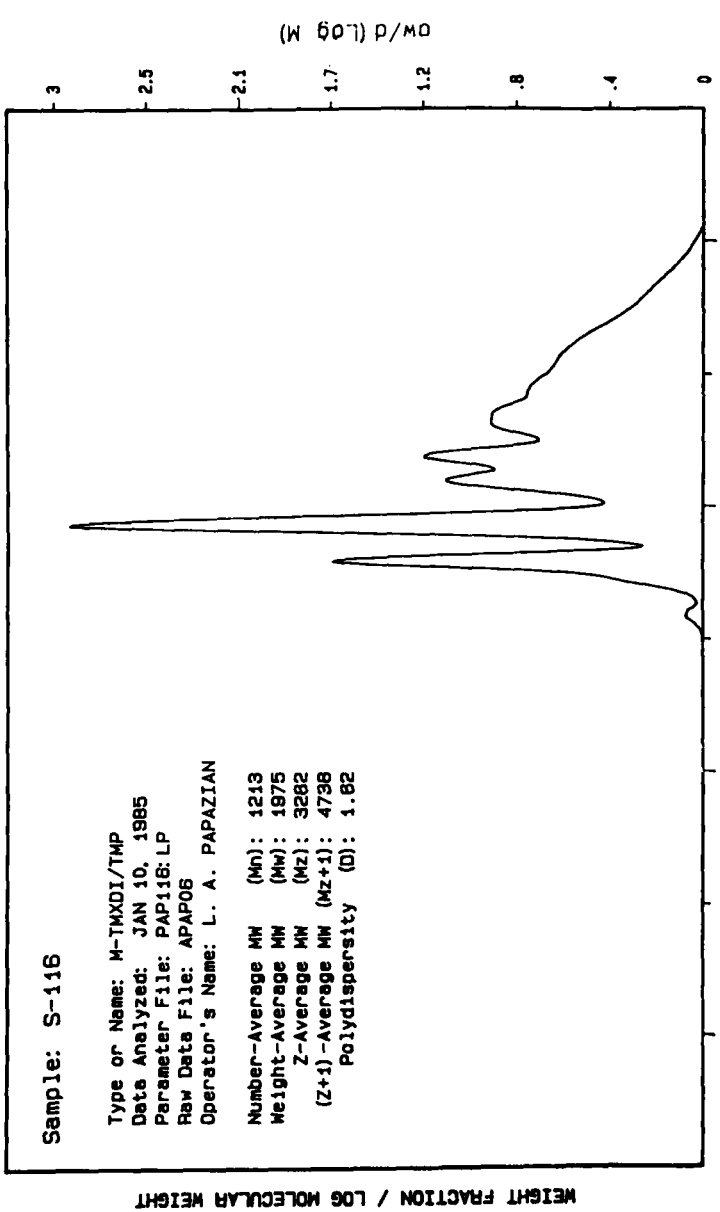


Figure 8: Differential Molecular Weight Distribution Curve for Sample S-116.

The number-average molecular weights, $\bar{M}_n$, in Table 2 indicate generally good agreement in level and trend with VPO data. In retrospect, this level of agreement is surprising since, in this calculation procedure, molecular weights are interpolated from the calibration curve every two seconds (the transfer rate) of the chromatogram. Simultaneously, one also assumes each well-resolved peak to be a single species. Other assumptions are that all components of a sample have the same refractive indices and no branched adducts exist in the reaction mixture. Nonetheless, this a approach does appear to provide consistent data of the proper magnitude.

The effect of molecular weight assignment with elution time can be demonstrated by shifting these assignments by one peak to either higher or lower elution time. For S-118, this results in $\bar{M}_n$ values equal 1550 and 650 g/mole, respectively. Since these values are beyond the limits of experimental accuracy (<5%) of the VPO method, one concludes that the major peak is indeed the 3/1 species. This proof, though indirect, is in agreement with expectation since the reaction is carried out with excess diisocyanate, and the 3/1 adduct should be the most abundant species.

A simpler and more rigorous method is available for calculating the molecular weights of these samples. By definition, the number-average molecular weight $\bar{M}_n$ is given by:

$$(1) \qquad \bar{M}_n = \frac{\sum C_i}{\sum C_i/M_i}$$

where C_i is the concentration of species with molecular weight M_i. Since peak areas of a chromatogram are proportional to concentration, equation (1) may be used for $\bar{M}_n$ calculations provided all species have the same response factor, i.e., the same refractive index. For the two typical urethane preparations

TABLE 3

$\bar{M}_n$ & Isocyanate Concentration Data

Technique:	HPSEC		Vapor Pressure Osmometry	Dibutyl Amine Titration
	$\bar{M}_n$[1] (g/mole)	NCO[2] Concentration (wt. %)	$\bar{M}_n$ (g/mole)	NCO Concentration (wt. %)
Sample				
S-78	949	14.4	1010	12.3
S-118	1020	14.2	1090	11.9

1. $$\bar{M}_n = \frac{\sum A_i}{\sum A_i/M_i}$$

2. $$\% \text{ NCO} = \frac{\sum A_i(\text{NCO})_i}{\sum A_i} \times 100$$

in this study, (samples S-78 and S-118), this calculation involves only six terms, in contrast to the more than 200 data points used by the earlier approach. These results in Table 3 are in excellent agreement with VPO data, and thus again support the assignment of the major peak as the 3/1 species. This calculation is not possible for the more complex chromatograms of the S-80 and S-116 samples. (These data were calculated from chromatograms obtained with the PLgel® columns.)

By an analogous calculation, the weight % isocyanate content (% NCO) was obtained from the relationship

(2) $$\% \text{ NCO} = \frac{\sum A_i(\text{NCO})_i}{\sum A_i} \times 100$$

In this equation, $(NCO)_i$ is the weight fraction of isocyanate of the i_{th} species having area A_i in the chromatogram. These results are also in agreement with independent titration data.

CONCLUSIONS

This study demonstrates the following:

1. With high performance SEC columns, "typical" m-TMXDI/TMP isocyanate adducts are well resolved at a molecular weight level of ~900 g/mole with both 10 μm and 5 μm particle size substrates in two solvents. As one may expect, the best separations are observed with the smaller particle size substrates. More complex preparations may also be quantitated with regard to the product distributions of these isocyanate oligomers.
2. Using methodology usually applied to high polymers, it is shown that both $\overline{M}_n$ and $\overline{M}_w$ may be calculated using the proper assignments of molecular weight to the peak elution times. These results agree in level and trend with vapor pressure osmometry. Thus, from one chromatogram, one can quantitate both the product distribution and also estimate molecular weight from truly internal standards (the distribution itself).
3. A simplified and more rigorous calculation of $\overline{M}_n$ for these new adducts is in excellent agreement with VPO data using only molecular weights and peak areas. This procedure is expected to provide very accurate and precise $\overline{M}_n$ (or $\overline{M}_w$) data for samples whose chromatograms contain well-resolved peaks.
4. Results of repeated HPSEC analyses illustrate the stability of these urethane oligomers.

ACKNOWLEDGEMENTS

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