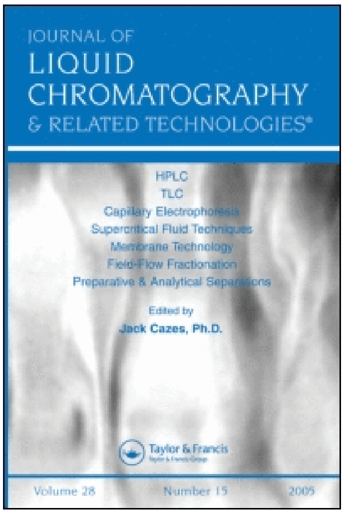

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THE ANALYSIS OF TOLUENE DIISOCYANATE AND DIPHENYLMETHANE DIISOCYANATE BY GEL PERMEATION CHROMATOGRAPHY

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ABSTRACT

A gel permeation chromatographic method was developed for the quantitative analysis of toluene diisocyanate and diphenylmethane diisocyanate in polyurethane polymers. Standard curves were linear over the range of concentrations 2-35 µg/mL and a good correlation was established between the amount of diisocyanate injected and the peak height. In addition to rapid quantitation of diisocyanate monomers, the method developed also separates the polyurethane prepolymers and diisocyanate dimers and trimers, allowing analysis of components of commercial samples in a single step.

INTRODUCTION

Polyurethane prepolymers are made by partially reacting isocyanate monomers, such as toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI) with active hydrogen containing

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compounds. These isocyanate monomers dimerize and trimerize with time. Therefore, the polyurethane prepolymers are very complex in structure, containing materials such as isocyanate monomers, biuret and allophanate, as well as, ether and ester containing oligomers.

Quantitation of monomeric isocyanates in polyurethane prepolymers is important for both quality control and safety. Most of the existing methods for the determination of isocyanate monomers involve derivatization followed by high performance liquid chromatography using reverse phase column (1-6). As far as the author is aware, there are only two articles on gel permeation chromatography of polyurethane prepolymers containing free MDI and TDI(7-8). Spagnolo and Malone(7) determined the amount of TDI in a polyurethane by derivatization of the sample with ethanol followed by gel permeation chromatographic separation. Bonart and Demmer(8) use gel permeation chromatography to study the nature of the polymer chain in a polyurethane.

In-house studies involving derivatization with n-butanol and subsequent reverse-phase liquid chromatography gave broad peaks for MDI and TDI when commercial samples were analyzed. Also under the conditions used, compounds with molecular weights higher than the monomers were not eluted. Therefore the chromatogram did not give any information about the components of a polyurethane prepolymer.

Gel permeation chromatography (GPC) has the potential to separate polyurethane prepolymer constituents based on molecular size, enabling one to separate monomer and polymer components in a single step. The present study is the first to describe the quantitation of MDI and TDI in polyurethane polymers, without derivatization, by means of gel permeation chromatography. In addition the analysis of mixtures containing both MDI and TDI by the method developed is described.

MATERIALS AND METHODS

i) Chemicals

Methylene chloride used was HPLC grade and was supplied by Caledon Laboratories, (Georgetown, Ontario). Diisocyanates (MDI and TDI) were supplied by Eastman Kodak (Rochester, New York). The samples analyzed were commercial products.

ii) Preparation of Samples

Diisocyanate standards of different concentrations were prepared by dissolving weighed amounts of the isocyanate in 10 mL of methylene chloride.

iii) Apparatus

Chromatographic analyses were performed using a Waters Associates Liquid Chromatograph equipped with a Model 6000 A Solvent Delivery System a Model 7125 Rheodyne Injector, a Waters R-401 Refractive Index Detector and a Laboratory Data Control Dual Pen Recorder.

iv) Separation Conditions

Separation was achieved using 500 A°, 100 A° and 100 A° Waters Styragel columns; 30 cm long, 7.8 mm ID. The mobile phase was methylene chloride at 1 mL/min flow rate, and the chart speed was 8 mm/min.

v) Quantitation

Ten μL of sample was injected and the results of these injections were averaged for each sample. An external standard method was used to determine percentages of MDI and TDI. Calibration curves for MDI and TDI were constructed from the peak heights of standard samples.

RESULTS AND DISCUSSION

Bonnart and Demmer used tetrahydrofuran for the analysis of polyurethane prepolymers(8). Their aim was to study the nature of the polymer chain (hard segments and soft elastomeric segments) and the accurate quantitation of MDI was not an important consideration.

Tetrahydrofuran absorbs moisture readily and thus could cause a decrease in the amount of isocyanate present. Moreover, our studies indicated that numerous commercial polyurethane prepolymers were not completly soluble in tetrahydrofuran. For these reasons methylene chloride was chosen as the solvent and eluent.

Figure 1 shows the chromatograms of the MDI and TDI standards. The solution containing both MDI and TDI has two well resolved peaks, indicating the potential of the method for quantitative analysis of samples containing both MDI and TDI.

The curves shown in Figure 2 and Figure 3 were constructed from the injection of known quantities of standard samples of MDI and TDI. The relationship between the peak height and concentration was linear within the range studied for both MDI and TDI. The correlation coefficients were 0.998 for MDI and 0.999 for TDI.

As mentioned earlier the isocyanates are very sensitive to water, amines and alcohols and they dimerize and trimerize with

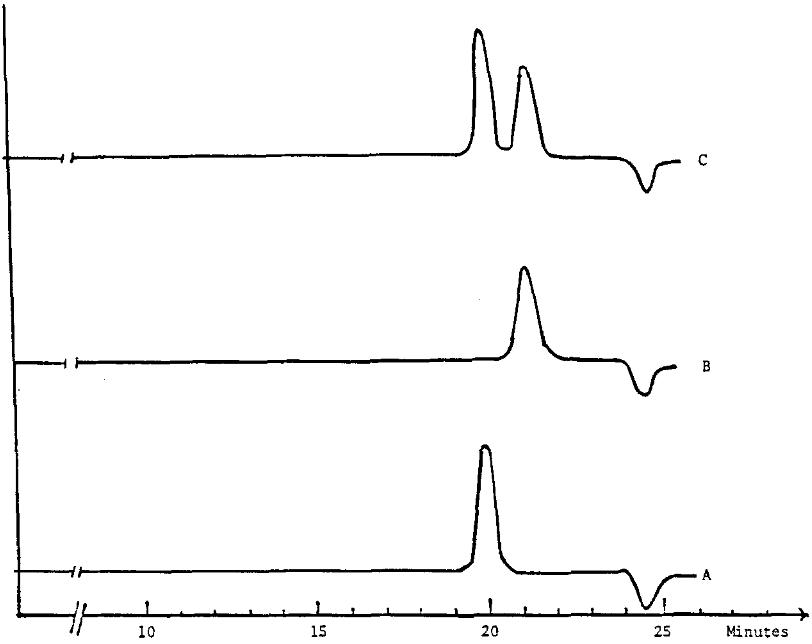

Figure 1 Chromatograms of MDI and TDI

A: Chromatogram of MDI

B: Chromatogram of TDI

C: Chromatogram of MDI and TDI

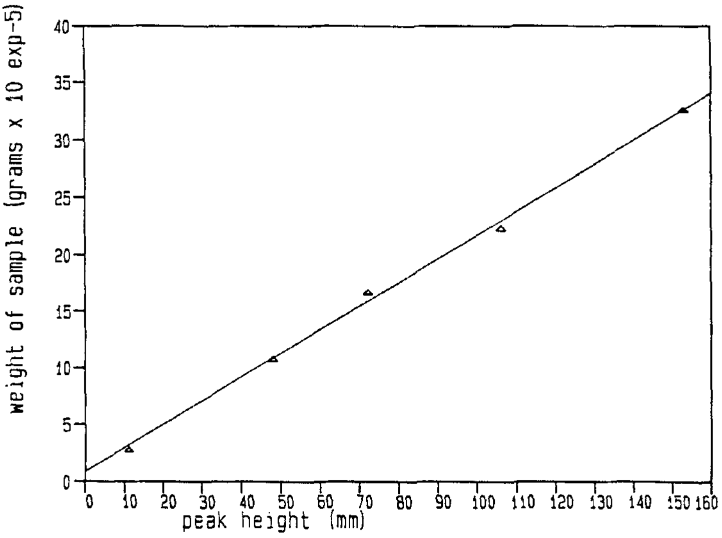

Figure 2 Standard curve for MDI

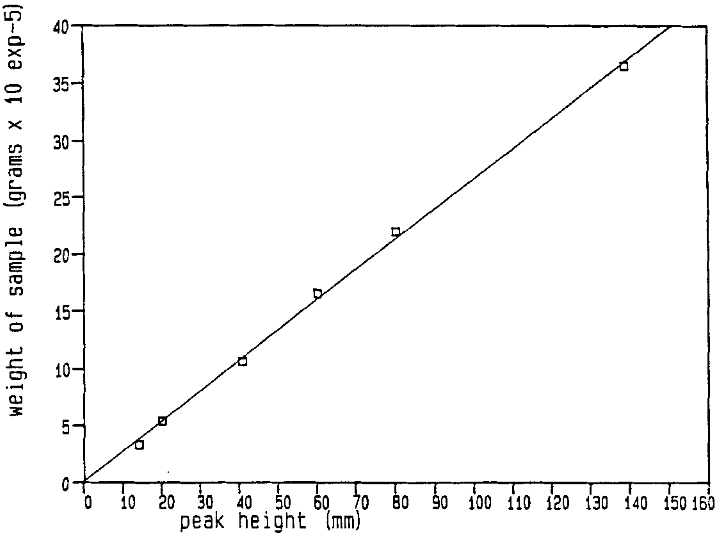

Figure 3 Standard curve for TDI

time. The analysis of commercial samples by the method developed allows determination of the extent of reaction as well as monomer quantity, in a single step without any work up and/or derivatization.

Representative chromatograms of commercial samples are shown in Figures 4-7. The chromatogram in Figure 4 is from a sample of crude MDI. This sample is found to contain about 43% of unreacted MDI, when analyzed by the method developed. In addition the same chromatogram shows the presence of other higher molecular weight constituents thus indicating the extent of the reaction.

The method developed allowed separation of a high boiling solvent (bp 180°C) present in a commercial sample (Figure 5). The presence of the solvent was not observable in the infrared spectrum.

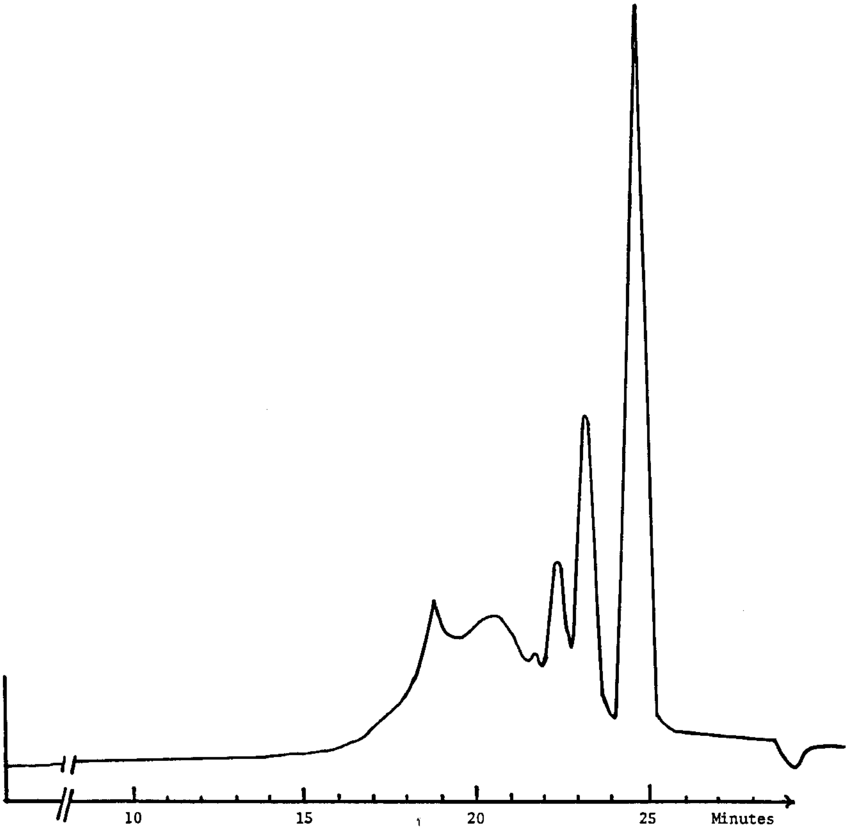

Figure 4 Chromatogram of crude MDI

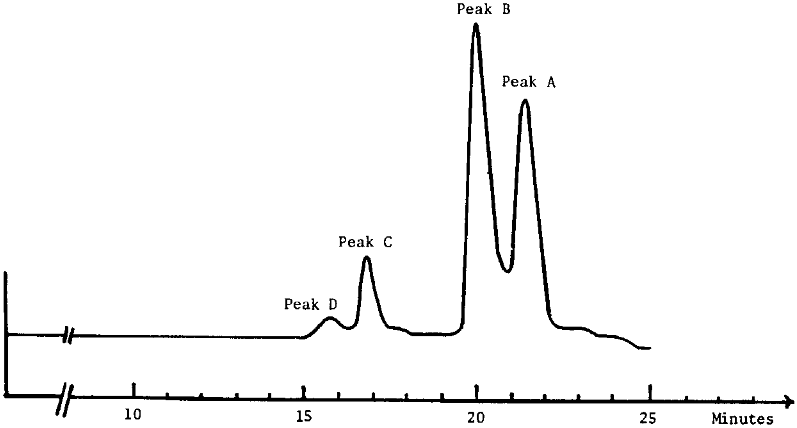

Figure 5 Chromatogram of a commercial polyurethane sample containing a hydrocarbon solvent

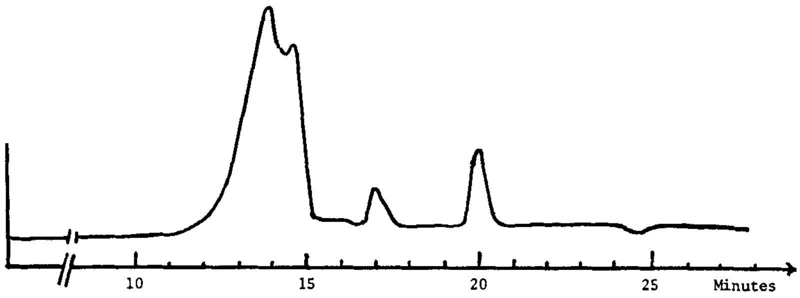

Figure 6 Chromatogram of a commercial polyurethane sample

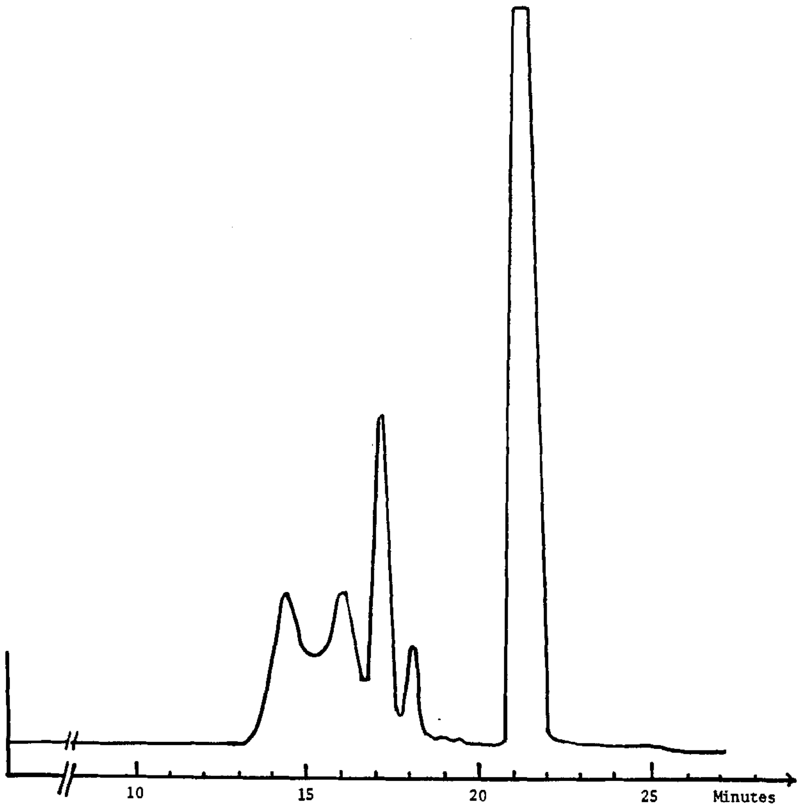

Figure 7 Chromatogram of a commercial polyurethane from TDI

The gel permeation chromatographic analysis revealed that the sample contained 30% by weight of a hydrocarbon solvent (Peak A) as well as separating MDI (Peak B) and higher molecular weight components (Peaks C and D). This was accomplished in a single step eliminating other lengthy procedures of separation. Thus,the method can also be used in determination of solvent content of polyurethane samples.

Figure 6 shows the chromatogram of a polyurethane sample with approximately 8% of unreacted MDI. A commercial sample containing free TDI was also analyzed by the method developed (Figure 7). The chromatogram shows the complexity of this material as well as enabling the TDI content to be determined.

In conclusion, the method described offers great simplicity and is potentially applicable to other isocyanate monomers used in polyurethane production. The contituents of a polyurethane prepolymer can be separated in one step. This paper is the first study reporting the quantitation of reactive monomers in a polymer by means of gel permeation chromatography without derivatization.

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