Note

Determination of free toluene diisocyanate in polyurethane prepolymers by high-performance liquid chromatography

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During the course of an investigation of the structure–property relationships of polyurethanes[1], it became desirable to have a method for determining the amount of free (monomeric) diisocyanate in urethane prepolymers because this determines the sequential distribution of the chains of the network or segmented polyurethanes. The need for such a method has also arisen in the urethane industry, as residual monomeric diisocyanates present in urethane prepolymers as a result of incomplete reaction or the use of non-stoichiometric amounts may yield toxic vapours in processing operations.

Although several methods for determining diisocyanate concentration in air are known[2–4], only a few studies have been concerned with the determination of free diisocyanate in urethane prepolymers. The methods proposed for separating monomeric toluene diisocyanate (TDI) are gas–liquid chromatography (GLC)[4–6], the ASTM method[7] and high-performance liquid chromatography (HPLC)[8,9].

GLC methods require high vaporizer and column temperatures for complete recovery and volatilization of diisocyanates. As a result, some degradation of the prepolymer may occur, which invalidates the results through liberating further TDI. The ASTM method is time-consuming and tedious. The use of HPLC may offer a means of overcoming the disadvantages involved in GLC and other methods by using a simple and rapid experimental procedure.

We have previously reported the quantitative analysis of several urethanes derived from TDI and 4,4'-diphenylmethane diisocyanate by HPLC[10]. This work was undertaken in order to determine quantitatively the fraction of free TDI in urethane prepolymers prepared from 2,4-TDI and poly(oxypropylene) glycol (PPG).

EXPERIMENTAL

Apparatus

A Model 634 high-performance liquid chromatograph (Hitachi, Tokyo, Japan) with a 254-nm ultraviolet detector and a refractive index detector was used. A 500 × 2.1 mm I.D. stainless-steel column was packed with Hitachi Gel 3010 (porous styrene–divinylbenzene copolymer). This packing was swollen in methanol and packed by the high-pressure slurry technique.

Preparation of polyurethane prepolymers

Polyurethane prepolymers were prepared from PPG and 2,4-TDI. PPG was supplied by Sanyo Kasei Industrial Co. (Kyoto, Japan). The number-average molecular weight of PPG was determined to be 1068 by vapour-pressure osmometry. 2,4-TDI was of commercial origin and purified by fractional distillation under reduced pressure (boiling point 89.8°C/3 mmHg). The purity was checked by the amine-equivalent method[11].

The prepolymers were prepared as follows. PPG, previously dried by passing dry air at 110°C, was weighed into a three-necked flask equipped with a nitrogen inlet and an outlet connected to a drying tube, thermometer and vacuum stirrer. The flask was heated to the required temperature in an oil-bath and then evacuated to degas the PPG. Various molar equivalents of 2,4-TDI ($K = [NCO]/[OH]$) were weighed accurately into the flask. The reaction mixture was stirred vigorously under a nitrogen atmosphere at 80°C. Reaction mixtures were sampled at regular time intervals and part of the sample was titrated by the amine-equivalent method in order to check the extent of reaction. The remainder was used for the preparation of the capped prepolymer.

Preparation of capped prepolymers

Isocyanate-terminated prepolymers were subjected to reaction with methanol at 40°C until residual isocyanate groups were completely converted into methyl urethanes. The capped prepolymers were dried under vacuum at 40°C until a constant weight was reached.

Preparation of standard solution

Purified 2,4-toluene dimethylcarbamate(2,4-TMU), which was prepared by reaction of 2,4-TDI with methanol, was used as a standard material. Standard solutions ($2 \cdot 10^{-4}$–$3.5 \cdot 10^{-2}$ mol/l) were prepared by dissolving a weighed amount of 2,4-TMU in methanol. These solutions were then submitted for analysis by HPLC.

Analysis of 2,4-TMU in capped prepolymers

Capped prepolymers (0.1 g) were weighed accurately and dissolved in 2 ml of methanol. The solutions were diluted to the range of concentrations covered by the calibration graph. A 3.0-μl volume of the solution was injected into the column via a septum by means of a microsyringe. Methanol was used as the mobile phase at a flow-rate of 1.0 ml/min at 21°C to separate 2,4-TMU and PPG-TDI adducts. This procedure was repeated five times on each sample solution.

Peak heights for 2,4-TMU on the chromatograms were determined manually. The concentrations of 2,4-TMU in the capped prepolymers were determined from their respective peak height and a calibration graph prepared by plotting peak height against 2,4-TMU concentration in the standard solutions. The concentrations of 2,4-TDI in the isocyanate-terminated prepolymers were calculated from

$$W = \frac{C_{TMU} \cdot \dfrac{\text{mol.wt. of 2,4-TDI}}{\text{mol.wt. of 2,4-TMU}}}{C \cdot \dfrac{1}{1 + 32.0 \, C_{NCO}}}$$

where

W = concentration of 2,4-TDI in the isocyanate-terminated prepolymer (g/g);

C_{NCO} = concentration of isocyanate group in the isocyanate-terminated prepolymer (mol/g), which was determined by the amine-equivalent method[11];

C = concentration of sample (the capped prepolymer solution) (g/ml);

C_{TMU} = concentration of 2,4-TMU in the sample (g/ml), which was determined from the calibration graph.

RESULTS AND DISCUSSION

A typical chromatogram for a capped polyurethane prepolymer is shown in Fig. 1. The chromatogram shows two major peaks, identified by comparing the retention time with that of 2,4-TMU (Fig. 1a) as (1) 2,4-TMU and (2) PPG–TDI adducts.
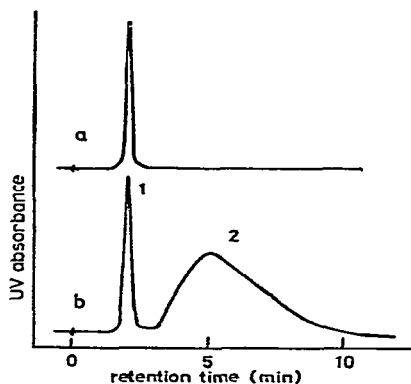

Fig. 1. Chromatogram of (a) 2,4-TMU and (b) polyurethane prepolymer. Peaks: 1 = 2,4-TMU; 2 = PPG–TDI adduct.

In previous work[10], the low-molecular-weight urethanes were separated satisfactorily with methanol–water (80:20) as the mobile phase, and the addition of water to methanol phase was therefore examined here. With increasing water content, the resolution between 2,4-TMU and the PPG–TDI adduct decreased. In this study, the resolution of the chromatogram using methanol as the mobile phase was 1.0–1.5.

In general, resolution affects the accuracy of measurement by the peak-height and peak-area methods. If the resolution is 1.0, the relative peak height can be varied from 32/1 to 1/32 with less than a ±3% variation in accuracy, but relative peak area can be varied only from 3/1 to 1/3. The accuracy of measurement by the peak-height method is better than that of the peak-area method at low resolution[12]. In this study, the peak-height method was employed for the determination of the concentration of 2,4-TMU.

The calibration graph for 2,4-TMU was linear up to 1800 ng and passed through the origin. The peak heights for a standard sample determined five times were

almost identical. Each amount of 2,4-TMU from 300 to 1800 ng injected in 3-μl volumes gave a point lying within $\pm 0.3\%$ of the calibration line. Under these conditions, the detection limit of 2,4-TMU was 80 ng, that is, the detection limit of free TDI in 3-μl volumes injected was 59 ng. This detection limit is 1.9 μg of free TDI in 0.1 g of a capped prepolymer.

In order to determine the reproducibility of the method, the determination of TMU in a particular sample of capped polymer ($K = 2.03$, 80°C, 45 min, see Table II) was repeated fifteen times. The results ranged from $3.290 \cdot 10^{-4}$ to $3.332 \cdot 10^{-4}$ mol/g in isocyanate-terminated prepolymer, with a mean of $3.31 \cdot 10^{-4}$ mol/g and a standard deviation of $1.65 \cdot 10^{-6}$ mol/g (*ca.* 0.5% of the mean).

As a test of the method, known amounts of 2,4-TMU were added to a capped prepolymer and total 2,4-TMU levels were determined. The results in Table I indicate that the method has an adequate reproducibility and that this method would be the preferred method for the determination of low levels of 2,4-TMU in capped prepolymers.

TABLE I

DETERMINATION OF 2,4-TMU ADDED TO CAPPED PREPOLYMER

Capped prepolymer: K = 2.03, 80°C, 35 min, see Table II.

2,4-TMU added (mol/l × 10⁷)	Total 2,4-TMU determined (mol/l × 10⁶)	Increment	
		mol/l × 10⁷	% *
0	4.930	0	0
1.01	5.031	1.01	100.0
2.02	5.137	2.07	102.0
4.04	5.332	4.02	99.5

* Ratio of increment to 2,4-TMU added.

In the method of Matsuura and Mukouda[9], PPG–TDI adducts were not eluted by an 89:11 mixture of *n*-hexane and 1,2-dichloroethane–methanol (2:1) and had to be separated by a gradient elution method. In the method of McFadyen[8], as the retention time of free TDI was same as that of the solvent (dioxane), a solvent correction was necessary for the determination of the TDI peak intensity. The method presented here overcomes these disadvantages.

By using the proposed method, the concentration of free 2,4-TDI was followed as a function of reaction time during the course of prepolymer formation at 80°C using an [NCO]/[OH] molar ratio of 2.03. The results are shown in Table II together with the extent of reaction based on the isocyanate group. The amount of free 2,4-TDI decreased with increasing reaction time. However, about 17% of the initial TDI still remained free at a 50% extent of reaction where the hydroxyl groups in the polymer glycol had reacted completely with isocyanate. In the sense of simple stoichiometry, or on average, every polymer molecule will be capped with two diisocyanate molecules at both chain ends at an [NCO]/[OH] molar ratio of 2.0. This means that free diisocyanate will not remain in the system.

This is not true, however, and a size distribution of molecular species will occur, as encountered in polycondensation. Alternatively, the extent of reaction based

TABLE II

VARIATION OF THE CONCENTRATION OF FREE 2,4-TDI IN PPG-TDI PREPOLYMER
$K = [NCO]/[OH] = 2.03$, $80°C$.

Time (min)	Extent of reaction (%)	Concentration of free TDI*	
		mol/g × 10⁴	%, w/w
0	0.0	14.34	24.97
15	15.0	8.31	14.47
35	37.5	3.64	6.33
45	43.9	3.31	5.76
60	45.4	3.18	5.53
90	48.7	2.70	4.70
125	50.0	2.49	4.33
180	52.2	2.22	3.86
240	60.3	2.08	3.61

* Ratio of 2,4-TDI to isocyanate-terminated prepolymer.

on isocyanate groups exceeded 50%, which means that isocyanate groups were substantially consumed by some reaction. Separate studies[13-15] on the structure of polyurethanes and prepolymers by the amine-degradation method indicated that the excess reaction can be attributed to allophanate formation. Hence result in Table II is considered to indicate that chain extension and allophanate formation occur during prepolymer formation. The detailed results of the characterization of polyurethane prepolymer obtained by the method presented here will be published elsewhere.

In conclusion, the HPLC method described offers great simplicity and applicability to other aromatic isocyanate for the determination of isocyanate in polyurethane prepolymers. Aliphatic isocyanates may be determined by this method by using a refractive index detector.

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