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Note

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

P. McFADYEN

Central Research and Development Division, Lankro Chemicals Limited, P.O. Box 1, Eccles, Manchester (Great Britain)

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Of the isocyanates available to the polyurethane industry, the most widely used is toluene diisocyanate (TDI) which is generally employed in the form of an 80:20 or 65:35 mixture of its 2,4- and 2,6-isomers. Since TDI has a toxic vapour and a viscosity which is too low for direct processing in certain applications, it is often used as a condensation product with a polyhydroxylic material, generally a diol or triol of molecular weight 60–5000. Although such "prepolymers" have a much lower vapour pressure and are more convenient to handle than TDI itself, they normally still contain a small amount of uncombined TDI which is difficult to remove except by costly distillation processes. It is therefore essential to have a convenient method for monitoring the level of residual TDI in these prepolymers in order to assess any potential toxic hazard in subsequent processing operations.

The ASTM method[1] for determining free TDI in low molecular weight polyurethanes involves vacuum distillation followed by reaction with sodium nitrite–2-ethoxyethanol reagent and subsequent colorimetric estimation. The method is time consuming and does not differentiate between TDI and other aromatic isocyanates. Gas–liquid chromatography (GLC) can be used[2–4] to determine free TDI but the column temperatures required for complete volatilisation of TDI are so high that some degradation of the prepolymer is possible. This liberates further TDI and invalidates the result.

Recent advances in high-performance liquid chromatography (HPLC) offer a means of overcoming these disadvantages using a simple and rapid experimental procedure. Having established the appropriate chromatographic conditions, only a few minutes are required for the analysis of each sample and since it is an ambient temperature technique, the problems associated with the GLC method are avoided. A suitable HPLC procedure for determining free TDI in a variety of urethane prepolymers is described below.

EXPERIMENTAL

An ALC 202 Liquid Chromatograph (Waters Assoc., Stockport, Great Britain) with ultraviolet (UV) absorbance (254 nm) and differential refractometer detectors was used with a 50 × 0.2 cm stainless-steel column packed with Corasil II

35–50 μm pellicular silica gel (Waters Assoc.) activated by heating at 110° for 12 h. A mobile phase consisting of isooctane (BDH Analar Reagent, 2,2,4-trimethyl-pentane, Product no. 30518) and 1,4-dioxan (BDH Analar Reagent, Product no. 10100) in the ratio 4:1 (v/v) gave satisfactory separations and was compatible with the highly reactive samples. These solvents were used without further purification other than drying over a molecular sieve. Constant flow-rates between 1 and 3 ml/min at ambient temperature throughout gave pressure drops in the range 500–2000 p.s.i.

Prepolymers were dissolved in dioxan at concentrations ranging from 1 to 10% (w/w) according to their expected free TDI levels and, typically, 4 μl of solution were injected onto the column. A standard 0.4% (w/w) solution of TDI in dioxan was used for calibration. It is not essential to use TDI of the particular isomer ratio used in making the prepolymer as there is no noticeable difference in detector response and, moreover, the isomer ratio of the uncombined TDI may differ from that of the starting material due to differences in reactivity.

Solutions (2–10 μl) were injected onto the column via a septum, the TDI standards being run immediately before and after each sample. An appropriate volume of dioxan was also injected in order to determine the solvent correction to be made to the TDI peak (see below). Finally, a correction was made for the UV absorbing solvents which were present in some of the prepolymers by injecting separate solutions of these. Results were calculated by comparing peak areas measured as peak height multiplied by peak width at half height.

RESULTS AND DISCUSSION

Nine TDI-based urethane prepolymers (Table I) were examined by the method and a typical chromatogram (prepolymer A) is shown in Fig. 1a. This illustrates all the major points of interest in the method. Prepolymer A is the reaction product of TDI and a mixed polyether polyol consisting of low molecular weight diol and triol

TABLE I

PREPOLYMERS USED

| Prepolymer	TDI–isomer ratio	Polyol type	Solids and solvent present (%)	Typical free-NCO (%)	Typical free TDI level (%)
A	80:20	Polyether, low MW diol and triol	80 (in MEK)	9	4–5
B	65:35	Trifunctional hydroxyl compound	75 (in ethyl acetate)	12	0–0.2
C	80:20	Polyether, high MW diol and triol	100	2.7–3.0	0.5–1
D	—	Polyether	100	2.7	1.4
E	80:20	Polyester diol (M.W. = 2000)	100	6.6	7.2
F	80:20	Polyester diol (M.W. = 2000)	100	5	5.2
G	—	Polyester	100	—	1.7
H	—	Polyether	100	28	37
J	80:20	Polyether diol	100	6.7	1
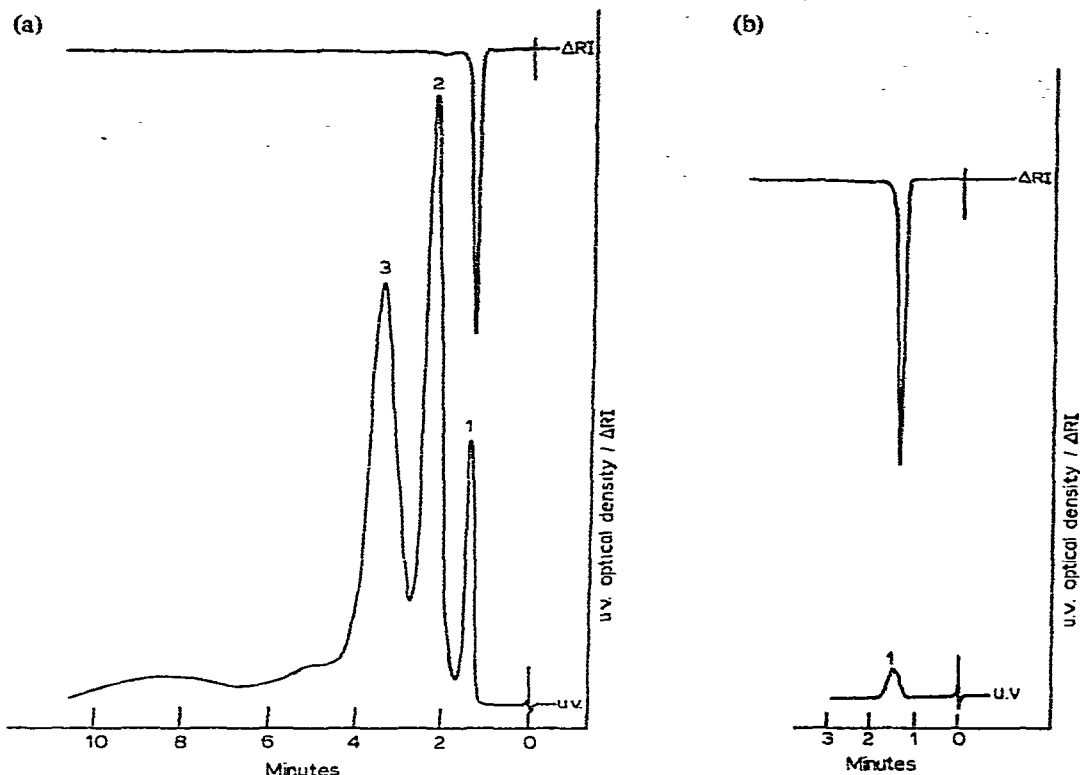
Fig. 1. (a) Chromatogram obtained for prepolymer A. Flow-rate, 3 ml/min. Peak identity: 1 = free TDI plus solvents; 2 = diol–TDI adduct; 3 = triol–TDI adduct. (b) Chromatogram of MEK and dioxan solvents. Amounts injected are equivalent to those included in (a).

and it contains 3–4% of free TDI. Also present is a UV absorbing solvent, in this case 20% of butan-2-one (MEK).

The chromatogram obtained using the UV detector shows three major peaks identified by comparing their retention times with those of individual standards as (i) TDI plus solvents, (ii) diol–TDI adduct and (iii) triol–TDI adduct. In addition there are minor peaks attributed to strongly retained, higher molecular weight condensation products. The free TDI is eluted on the solvent front together with the dioxan and MEK. These components could possibly have been resolved by using a less polar solvent but this was precluded by the need to elute the more strongly retained components in order to preserve constant column characteristics. Gradient elution might have been useful here but was not available for the present work. As can be seen from Fig. 1b, the dioxan and MEK contribute only a minor amount to peak (i). The correction for these was simply made by separately injecting suitable volumes of dioxan and a standard solution of MEK in dioxan and subtracting from the TDI peak areas in both sample and standard chromatograms the appropriate solvent contribution. In the particular case illustrated in Fig. 1, the total solvent correction amounted to 6.5% of the area of peak (i).

Injecting under high pressure via a septum has the disadvantage that it is

difficult to obtain high accuracy and repeatability of injection volumes. One means of overcoming this is to incorporate an internal standard at equal concentration in both sample and standard solutions. Often, however, when dealing with urethane prepolymers the wide range of retention times of the various components leaves no room in the chromatogram for such a standard. Alternatively, the large number of injections required to obtain a reliable value of the injection volume without the use of an internal standard would be very time consuming thereby eliminating one of the chief attractions of the method. However, the simultaneous use of two detectors offers the following solution.

The UV detector is operated at fairly high sensitivity to obtain the actual chromatogram leaving the differential refractometer available to measure the injected volume. Typically, 4 μl of 1 % (w/w) prepolymer solution in dioxan are injected; thus, for a prepolymer which contains 5% free TDI and 20% MEK, the initial peak is due to 2 μg TDI, 8 μg MEK and 4,120 μg dioxan. The larger amount of dioxan present easily outweighs any differences in refractive index (RI) of these components and the refractometer therefore responds almost wholly to the dioxan. Thus, by using the differential refractometer at a low sensitivity, a single on-scale peak is obtained which can be used as a measure of the sample volume injected. For high accuracy work, the very small contribution of the TDI and MEK to the RI peak can be calculated from an approximate analysis based on the nominal injection volume indicated by the syringe and an allowance can then be made in calculating the true injection volume.

As a test of the complete method, known amounts of pure TDI were added to several urethane prepolymers and total free TDI levels determined. The results (Table II) indicate that the method is applicable to prepolymers of widely differing free TDI contents. This standard addition method followed by extrapolation to zero addition of TDI would be the preferred method for the determination of low levels of free TDI as, for instance, in the case of prepolymer B.

As a measure of the reproducibility of the method, thirteen determinations of

TABLE II

STANDARD ADDITION OF TDI TO PREPOLYMERS

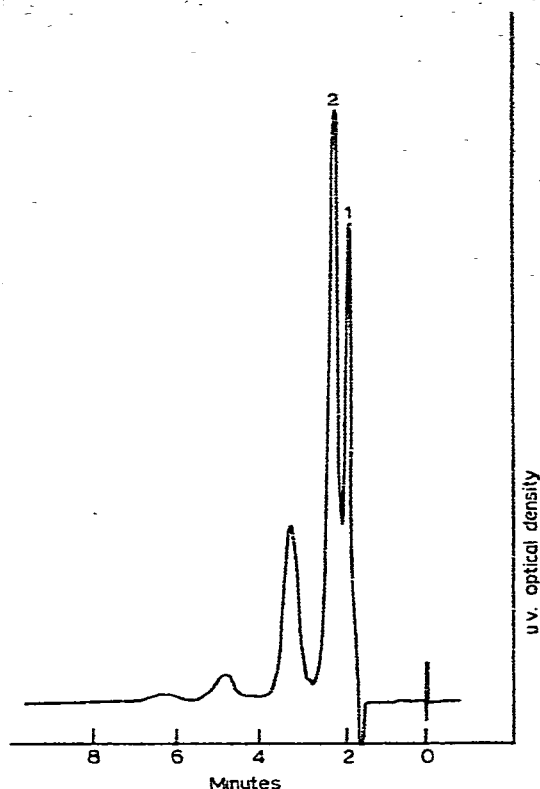| Prepolymer	TDI added (%)	Total TDI determined (%)	Increment (%)
A	0.00	3.2	—
	3.0	6.3	3.1
	4.7	8.0	4.8
	9.0	11.0	7.8
B	0.00	0.22	—
	0.50	0.72	0.50
	0.97	1.24	1.02
	1.95	2.39	2.17
	2.97	3.39	3.17
	3.98	4.43	4.21
H	0.00	37.3	—
	24.6	60.1	22.8

Fig. 2. Chromatogram obtained for a prepolymer based on mixed isocyanates. Mobile phase, 1,2-dichloroethane–isooctane (4:1). Peak identity: 1 = TDI; 2 = MDI.

free TDI in a particular sample of prepolymer J were made. These ranged from 0.975 to 1.152% with a mean of 1.067% and a standard deviation of 0.054, approximately 5% of the mean value.

With modified solvent mixtures usi .g 1,2-dichloroethane instead of dioxan, the method has been applied to 4,4'-diphenylmethane diisocyanate (MDI) in both MDI–TDI blends and prepolymers based on these isocyanates. MDI is eluted immediately after TDI and no solvent correction is necessary for calculating free MDI levels. Fig. 2 shows a chromatogram obtained for a prepolymer based on an MDI–TDI blend and a low proportion of polyol.

ACKNOWLEDGEMENTS

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