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Determination of Poly(oxypropylene Diol) Present in Poly(oxypropylene Triol) by Thin-Layer Chromatography

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Synopsis

A thin-layer chromatographic method has been developed for the quantitative determination of poly(oxypropylene diols) present in poly(oxypropylene triols). The polyols are separated on silica gel plates in a modified developing chamber using ethyl acetate as the developer. Quantitative results were obtained by conventional visualization and densitometer techniques. Polyols ranging in average molecular weight from 400 to 3000 have been resolved by this method. Diols present in a mixture with triols can be detected at levels as low as 1.0%.

INTRODUCTION

Some physical properties of flexible polyurethane foams made from poly(oxypropylene triols) are influenced by the presence of poly(oxypropylene diols). Per cent elongation, compression load deflection (CLD), and indentation load deflection (ILD) are among those affected. The amount of diol present in the triols is determined by the level of water present in the polymerization process. Thus, while a knowledge of this parameter can yield a calculated value, it is of importance for characterization purposes to have available an analytic method for the determination of weight per cent diol in the presence of triol.

Conventional methods such as gas chromatography[1] and liquid-phase chromatography[2] have been useful in the separation and identification of some short-chain polymeric diols according to their molecular weight. Recently, it has been found that thin-layer chromatography (TLC) is a novel technique for the separation of some high molecular weight hydroxylated compounds according to differences in molecular weight. To date, the TLC techniques described in the technical literature for the separation of polyols consist of the following types: (a) conventional TLC,[3] (b) conversion of the polyols to the acetylated ester prior to TLC,[4,5] and (c) conversion of the polyols to 3,5-dinitrobenzoate derivatives prior to TLC.[6] Other techniques reported the modification of the adsorbent with a complexing agent such as boric acid[7] and $Pb(NO_3)_2$.[8] In each reported case,

the TLC method was applicable only to poly(oxyethylene diols) wherein the polymers were separated qualitatively only by molecular weight.

Through the use of the TLC method to be described, a quantitative determination can be made on the amount of diol present in the triol even though the molecular weight range of the two types of compounds may overlap. Concentrations as low as 1.0 wt-% diol in triol can be accurately obtained.

EXPERIMENTAL

Apparatus

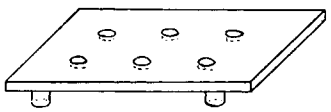
Thin-Layer Plates. Silica gel (type Silicar 7G by Mallinckrodt)-precoated plates, by Analtech, were employed. These plates were used as received from the supplier. No equilibration time was needed.

Syringes. Hamilton 10-μl syringes were used.

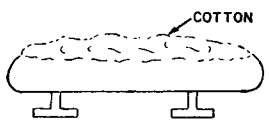
Chromatographic Chamber. A standard Brinkman Chamber ($8^1/_2 \times 4^1/_2 \times 8^1/_2$ in.) was slightly modified (Fig. 1). A perforated glass plate with four legs was fabricated and inserted into the chamber to hold the TLC plate above the water that is saturating the ethyl acetate solvent. If the TLC plate is not separated from the water level, the adsorbent has a strong tendency to flake off of the plate after development. In order to maintain a high level of water saturation inside the tank, a glass trough is filled with adsorbent cotton and saturated with distilled water. After the solvent and "saturator" trough are placed into the tank, the system is equilibrated for 64 hr.

Chromatographic Sprayer. John spray bottle to spray the plates.

Services. An electric hot plate was set in a hood to remove any acid fumes generated on visualization of polymers.



GLASS BASE PLATE



GLASS CHAMBER SATURATOR

Fig. 1. Perforated Pyrex base plate and chamber saturator trough located in developing tank.

Densitometer. A Photovolt densitometer (Model 520M, Photovolt Corporation, New York) equipped with a motor-driven TLC stage, a Varicord 42B recorder, and a Search Unit B.

Reagents

Visualizer. Concentrated sulfuric acid, as supplied, was used for the destructive visualization.

Developer. A water-saturated ethyl acetate solution was prepared by adding 30 ml of distilled water to 170 ml of ethyl acetate. The two solutions were vigorously contacted for 2 min and total volume was added to the developing tank. The insoluble water, on standing, collected in the bottom of the tank below the glass platform.

Standard Solutions. Mixtures totaling 1.0 ± 0.05 g of the diol and triol were weighed into 10-ml volumetric flasks. These samples were solubilized by adding chloroform to the mark. The concentration of the polymeric mixture was then about 100 μg per microliter. Several of these solutions were prepared in increments of 5% diol in triol.

Chromatographic Procedure

The sample and calibration compounds are spotted on the precoated TLC plates sized 10 × 20 cm and 250 μ thick. No special handling of the plates is necessary aside from keeping them stored in the packing container. In very humid locations it may be necessary to store these plates in a desiccated cabinet. If the range of the diol present in the triol product is not known, it is necessary to spot several of the known mixtures along with the sample on the plate. A 1–2 μl (100–200 μg) application of sample gives the best spot reproduction. In applying these small amounts of liquid to the TLC plate, the use of warm air from a hot air source is not needed. This could result in spattering or creep-back, increasing the chances of getting nonreproducible spots. Three spots of sample are applied to the plate alternating with three spots of the selected standard. The plate is then placed into the developing tank and the liquid front is allowed to travel 13 cm from the point of sample application. Total developing time is 35 min. The developed plate is then removed and allowed to air dry in the hood. When dry, the plate is sprayed with concentrated H_2SO_4 and the plate is then placed on a hot plate or in an oven. The temperature is set at 110°C and the time for charring is about 30 min. Higher temperatures should yield faster charring times. It is recommended not to place a TLC plate directly onto a hot plate surface because this practice usually leads to a shattered TLC plate. After the plate has been thoroughly charred, it is analyzed by densitometry.

The densitometer has a variable slit system installed as described by Blank.[9] After the diol spots are scanned and recorded, the diol peak (Fig. 2) is then baselined and cut out, using either a scalpel or razor blade, and weighed on an analytical balance. The procedure is repeated for each of the diol peaks. Occasionally, when rogue values appear, these are

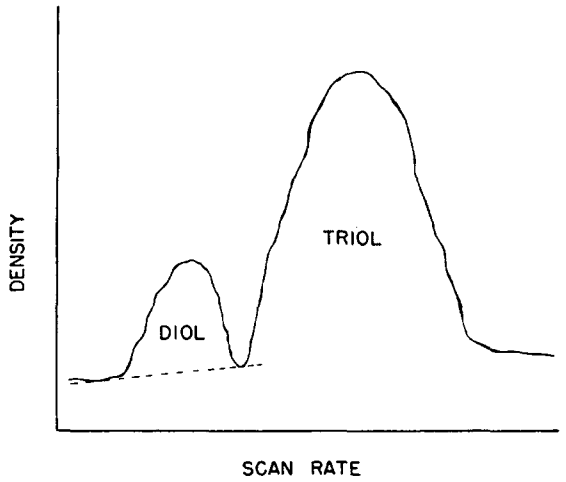


Fig. 2. Typical densitometric scan of TLC-separated poly(oxypropylene diol and triol), using a Photovolt recording densitometer.

discarded and not used. If all three readings do not agree within 5%–10% of each other, the analysis should be repeated. The per cent diol is calculated as follows:

$$\% \text{ diol} = \frac{A_u \cdot W_s}{A_s / W_u}$$

where A_u = weight of unknown diol peak, A_s = weight of known diol peak, W_u = weight of unknown deposited in plate, and W_s = weight of known deposited in plate.

RESULTS AND DISCUSSION

This technique deals with the separation of specific polyols by the number of functional groupings, i.e., diol from triol. In the course of developing this procedure, many solvent systems were investigated, including published systems. Some of these systems would separate the diol from the triol sufficiently to give a qualitative inspection. However, in order to quantize the separation, the two compounds must have a large enough R_f value between them, so that accurate densitometer readings can be obtained. The key to this separation is to maintain a water-saturated atmosphere in the tank. To satisfy this condition as described above, a small glass trough (Fig. 1) is filled with absorbent cotton, saturated with distilled water, and kept in the glass developing tank.

The colorless compounds, after development, can be visualized with a modified periodate–rosaniline hydrochloride reagent[10] which imparts a purple color to the spots. However, for analysis, the stability of these colors is of a short duration. Sulfuric acid-charred TLC plates, on the other hand, can be analyzed several hours later with little or no change in

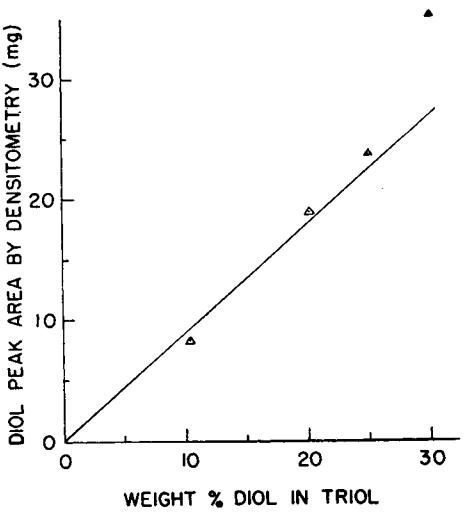


Fig. 3. Diol concentration vs. densitometer measurement, after TLC separation of synthetic blends.

the density readings. Also, if desired, a photograph can be taken of this TLC plate as a permanent record of the separation.

Good agreement was found to exist between the measured diol areas on the charred TLC plate and the actual amount applied. Figure 3 shows that linearity exists in the range of 0%–25% diol in triol but falls off sharply above this range. This is due to the fact that all of the values in the 0%–25% range were measured under a preselected slit program. In order to measure in the range above 25%, the slit should be adjusted along with the sample charge to regain linearity. The technique outlined in the procedure was applied to the determination of several synthetic mixtures of commercially available polyols having an average molecular weight of 2000. The concentration of the diol ranged from 0–25 wt-%. The data shown on Table I indicate that there was excellent agreement between the known values of those determined by this method.

TABLE I
Determination of Added Diol in Commercial Triol[a]

	Diol, wt-%		
Sample no.	Known	Found	Mean Error
1	5.71	5.40	−0.30
2	11.08	10.56	−0.52
3	15.20	14.80	−0.40
4	20.50	20.70	+0.20
5	25.50	24.90	−0.60

[a] Average mol wt 2000.

TABLE II
Diol Content in Some Laboratory-Prepared Triols

Sample no.	H_2O added, mole-%	Diol found, wt-%	
1	6.0	1.2	av. 1.3
2	6.0	1.4	
3	26.7	16.3	av. 16.9
4	26.7	17.6	
5	27.0	16.6	av. 17.3
6	27.0	18.0	
7	27.6	17.0	av. 17.9
8	27.6	18.9	

Several laboratory-prepared polyols, M_w/M_n = 2950/2700 (determined by gel permeation chromatography using styrene as a standard), were studied. In the formulation process, known amounts of water were added to vary the amount of the diol formed. The results of the TLC analyses are shown in Table II. For example, where an overall average of 27 mole-% total water is added in the formulation, an average of 17.6 wt-% diol is produced. Several available commercially produced triols were inspected by this method. Table III contains the results of the analyses, indicating a diol concentration ranging from 3.0% to 9.0%. These are averages of nine determinations for each product. After this practical application of the method, the procedure was then extended the full range of available molecular weight polyols. Figure 4 shows a developed TLC

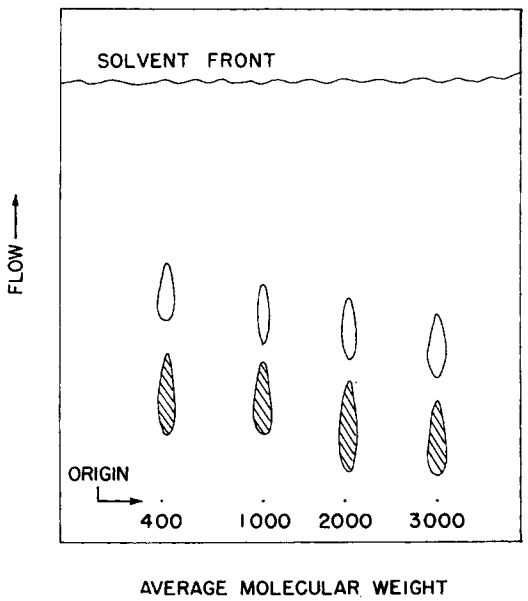


Fig. 4. Separation of mixtures of diols (white spots) and triols (hatched spots) ranging in average molecular weight from 400 to 3000.

TABLE III
Analyses of Some Commercially Available Triols

Sample	Diol found,[a] wt-%
Dow (CP 3000)	9.6
Wyandotte (GP 3030)	3.0
Union Carbide (LG-56)	2.9
Jefferson (Thanol F-3000)	9.9

[a] Average of nine determinations.

plate with four polyol mixtures ranging in molecular weight from 400 to 3000. The results of the separation indicate the versatility of the separation technique.

In general, the TLC densitometric analysis appears to be of potential use for the quantitative analysis of the polyols. It is both a sensitive and relatively simple method of analysis. With a large developing tank, it is possible to analyze several samples simultaneously and give results in a short elapsed time.

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