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THIN-LAYER CHROMATOGRAPHY OF THE LINEAR OLIGOMERS OF ETHYLENE TEREPHTHALATE

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SUMMARY

A method for the qualitative and quantitative analysis of the linear oligomers of the ester–diol type and ester–hydroxy acid type from ethylene terephthalate is described. As thin-layer chromatographic solvent systems, a chloroform–ethanol (9:1) system is suitable for the separation of the oligoesters of the ester–diol type and a *n*-propanol–28% aqueous ammonia–water (70:25:5) system for the ester–hydroxy acid type. Oligoesters separated on the thin-layer chromatographic plate were sprayed with a hydroxylamine solution and then with a ferric perchlorate solution, so that purple chelate complexes were formed. Quantitative analysis was carried out by lifting the spots from the plate, reacting them again with the same two solutions, and, after filtration, measuring the absorption of the solution at 540 nm.

The average recovery was 97%. The method could decrease the experimental errors caused by scraping off the spots, because visible spots were scraped and unreacted samples were again reacted with the same reagents.

INTRODUCTION

Polyethylene terephthalate (PET) prepared by polycondensation of dimethyl terephthalate and ethylene glycol contains some oligomers as equilibrium products. The oligomers were first isolated from PET by Ross *et al.*[1] and the existence of the cyclic trimer, tetramer, pentamer and pseudo-dimer were confirmed by GOODMAN AND NESBITT[2,3]. Although linear oligoesters were not detected in PET, there were a few reports on the syntheses of model compounds and their separation. ZAHN AND KRZIKALLA[4] prepared three homologous series of linear oligoesters of terephthalic acid and ethylene glycol (ester–diols, ester–dicarboxylic acids and ester–hydroxy acids) and separated them on a paper chromatogram. The oligomers of the ester–diol type ($n = 1$–4) were separated on a thin-layer chromatogram of Kieselgel HF 240 using two different solvent systems, *viz.* tetrachloroethane–dioxan (10:1) and benzene–dioxan (1:1) (ref. 5). PYL AND WUNTKE[6] reported the qualitative and quantitative analysis of oligomers of the ester–diol type ($n = 1$–7) by thin-layer chromatography

(TLC) and column chromatography. They prepared TLC plates of Aluminium Oxide D and used chloroform–ethanol (97:3) as a mobile phase. Each spot separated on the thin-layer chromatogram was scraped off after detection with a potassium permanganate–concentrated sulphuric acid solution. The esters in aluminium oxide were saponified with sodium hydroxide and the sodium terephthalate liberated was precipitated with lead acetate as an insoluble lead salt, followed by gravimetry. The separation of oligomers of the ester–hydroxy acid type has not yet been reported.

In the present work, oligomers of the ester-diol type ($n = 1$–4) and ester-hydroxy acid type ($n = 1$–3) were separated by TLC and good separation results were obtained. In quantitative analysis, each spot was scraped off from the plate after colour development of the spots by means of the hydroxamate method[7] on chromatographic plates, dissolved in methanol and colour development was then carried out again by means of the hydroxamate method. After filtration, the absorption of the solution at 540 nm was measured. The sensitivity of the colorimetric method is higher and operations are simpler than in the gravimetric method. Direct densitometry is also discussed.

EXPERIMENTAL

Materials

Mono-, di-, tri- and tetrameric oligomers of the ester–diol type and mono-, di- and trimeric oligomers of the ester–hydroxy acid type were synthesized according to the procedures described by HASHIMOTO[8] and ZAHN AND KRZIKALLA[4]. The former oligomers were dissolved in tetrachloroethane, and the latter in dioxan to give a 1 % concentration.

Thin-layer chromatography

Thin-layer plates (250 μm thick) were prepared by the usual method, using "Wakogel" B-5 (silica gel for TLC containing about 5 % of calcium sulphate) on 20 × 20 cm glass plates. The plates were activated at 110° for 1 h and stored over a silica gel desiccant until used. Solvent systems used were: (A) chloroform–ethanol (97:3) and (B) chloroform–ethanol (9:1) for the ester–diol type oligomers, and (C) *n*-propanol–28 % aqueous ammonia–water (70:25:5) for the ester–hydroxy acid type oligomers.

Qualitative analysis

About 8 μl of the sample solutions were spotted on the TLC layer by means of a micro syringe and the plates were chromatographed until the solvent front ascended 10 cm from the spotting point in a closed, saturated chamber using one of the above solvent systems. After chromatography, the plates were sprayed with a solution of 0.5 g of potassium permanganate in 15 ml of concentrated sulphuric acid[6]. The spots to be identified were white on a purple background.

Quantitative analysis

50–500 μl (0.5–5 mg) of the sample solution were spotted zonally on the plates and chromatographed. Solvent system B was used for the ester–diol type and C for the ester–hydroxy acid type.

Colour development reagents were prepared by the following procedures[7].

(1) *Alkaline hydroxylamine reagent.* This was prepared by mixing equal volumes of 12.5 % hydroxylamine hydrochloride in methanol and 12.5 % sodium hydroxide in methanol and filtering off the precipitated sodium chloride.

(2) *Ferric perchlorate reagent.* This was prepared by dissolving 0.16 g of iron powder in 2 ml of perchloric acid, transferring the contents to a 500-ml volumetric flask with 2 ml of water, adding 6 ml of 70 % perchloric acid and diluting to volume with ethanol.

After chromatography, the plate was sprayed with reagent 1 and heated at 70° for 20 min in an oven. After cooling, the plate was sprayed with reagent 2. The purple chelate complex that formed on the plate with the esters was removed with the surrounding support into a 25-ml flask. In order to complete the above reaction, 5 ml of ethanol and 3 ml of reagent 1 were added to the flask and the solution was refluxed for 20 min and then 30 ml of reagent 2 were added. The silica gel was filtered off and washed with ethanol, and the filtrate was diluted to volume with ethanol in a 50-ml volumetric flask. The absorbance of the solution was measured at 540 nm against the reagent blank (Hitachi spectrophotometer, model 124). The concentrations of each component were calculated by means of the calibration curve which was constructed using the monomer of the ester–diol type.

RESULTS AND DISCUSSION

Qualitative analysis

Several mixtures of polar and non-polar solvents were examined and only three solvent systems, A, B and C, gave good results.

Table I shows the R_F values of the species in the different solvents. PYL AND WUNTKE[6] had used solvent system A in the separation of the oligomers of the ester–diol type up to the heptamer, but solvent system B was better suited for the separation of the esters of lower molecular weight (n = 1–4). Solvent system C gave good results for the separation of the oligomers of the ester–hydroxy acid type.

Quantitative analysis

The maximum absorbance of the ferric hydroxamate complexes against the reagent blank was obtained at 540 nm and the absorbance at 540 nm reached a maxi-

TABLE I

TLC R_F VALUES OF THE LINEAR OLIGOESTERS OF THE ESTER–DIOL TYPE AND THE ESTER–HYDROXY ACID TYPE

Compound	*Solvent system*		
	A	*B*	*C*
Diol-monomer	0.16	0.32	0.70
Diol-dimer	0.26	0.45	0.71
Diol-trimer	0.33	0.53	0.71
Diol-tetramer	0.38	0.71	0.73
Hydroxy acid-monomer	0.30	0.73	0.30
Hydroxy acid-dimer	0.30	0.74	0.55
Hydroxy acid-trimer	0.40	0.74	0.60

TABLE II

DIOL-MONOMER ANALYSIS

No.	*Sample taken (mg)*	*Found (mg)*	*Recovery (%)*	*Absorbance (2.50 mg/50 ml)*
Accuracy				
1	1.60	1.51	94.4	
2	1.60	1.59	99.4	
3	1.37	1.33	97.1	
4	1.37	1.29	94.2	
5	1.37	1.33	99.3	
Average			97	
Precision				
1				0.493
2				0.500
3				0.482
4				0.502
5				0.484
6				0.498
7				0.479
Average				0.491
S.D.				±2.0%

mum after refluxing for 15 min. Coloured ferric hydroxamate complexes were stable for at least 12 h. The calibration curve was linear in a region 10–80 μg/ml. This method could decrease the experimental errors brought about by scraping off the spots, because visible spots were scraped and the reaction was carried out again with the same reagents. The data in Table II show that the mean recovery of the method was 97 % with a standard deviation ± 2 % for the analysis of the ester–diol monomer.

The absorbances of the complexes of the diol-monomer, -dimer and -trimer with the same concentration were measured, and the results are given in Table III, in which the concentration of each solution is expressed as mequiv./100 ml, so that each solution contains the same number of the ester groups. The absorbances of the complexes of the diol-dimer and -trimer per ester group are almost the same as that of the diol-monomer. Even though the diol-dimer and -trimer are insoluble in ethanol, they become soluble by refluxing them with reagent 1. During refluxing, each ester group is attacked by hydroxylamine, and the ester bond is cleaved and reacts with hydroxylamine. Accordingly, a calibration curve for the monomer is available for the determination of the concentration of the dimer and trimer.

Direct densitometry was also examined. The thin-layer plates employed were commercial silica gel layers on plastic films. After chromatography and colour development, the films were cut into long, narrow strips of 2 cm width in the direction of the solvent flow and covered with a cellophane tape. A Shimazu spectrophotometer, Model QR-50, equipped with a paper chromatographic stage was used. The absorbance of each spot was read at intervals of 1 mm on the strip and plotted as absorbance *vs.* the distance from the starting point. The ratio of each peak area to

TABLE III

COMPARISON OF THE ABSORBANCES OF DIOL-MONOMER, -DIMER AND -TRIMER

Concentration (mequiv.[a]*/100 ml)*	*Absorbance*		
	Monomer	*Dimer*	*Trimer*
5.0×10^{-2}	0.610	0.585	0.573
5.0×10^{-2}	0.615	0.640	0.545
5.0×10^{-2}	0.609	0.595	0.560
5.0×10^{-2}	0.606	0.610	0.584
Mean absorbance	0.610	0.607	0.566
Ratio to monomer	1.000	0.995	0.927

[a] 1 mequiv. of the diol-monomer per ester group is 127 mg, of the diol- dimer 112 mg, and of the diol-trimer 106 mg.

the total peak area is the ratio of each component in the sample. The direct densitometry method had a larger standard deviation of ± 8.5 % than the above method. If an automatic aparatus for direct densitometry is available, the standard deviation of this method will decrease and the operation will be simplified.

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