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GAS CHROMATOGRAPHIC ANALYSIS AFTER DEGRADATION OF COPOLYETHER POLYESTERS

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SUMMARY

A method has been developed for the analysis of copolyether polyesters, based on chemical cleavage by transesterification followed by gas chromatography. The 1,4-butanediol and polyether parts were acetylated prior to gas chromatography. It was thus possible to differentiate between the butanediol originating from the soft, polyether part and that resulting from the hard segment of the copolyether polyester. Pyrolysis–gas chromatography was found to be eminently suitable for a preliminary identification of the copolyether polyester and its differentiation from poly(1,4-butanediol terephthalate).

INTRODUCTION

The copolyether polyesters form part of a new class of rubbers which combine the elastomeric properties of vulcanised rubber with thermoplasticity and are termed thermoplastic elastomers (TPE). At room temperature they are elastomers, while at elevated temperatures they do not decompose as vulcanised rubbers do, but are processable and may be recycled like thermoplastics.

Copolyether polyesters, obtained by modification of polyethylene terephthalate with up to 20 percent by mass of polyethylene ether glycol, were first reported by Coleman[1] and by Snyder[2]. Shivers[3,4] introduced other polyalkylene ether glycols and used them in much higher quantities in combination with the polyester segment, obtaining a broad range of polymers, varying from hard to highly elastic products. Subsequently, the Du Pont company developed these copolyether esters, which were commercially introduced in 1972 under the trade name "Hytrel".

The copolyether polyesters are prepared from dimethyl terephthalate, poly(1,4-butylene ether glycol) and 1,4-butanediol by copolycondensation[5]. Their structure is considered to be formed by randomly joined soft and hard segments:

$$\left[(O-CH_2CH_2CH_2CH_2)_x - OCO - \langle\bigcirc\rangle - CO\right]_n \quad \left[O-CH_2CH_2CH_2CH_2 - OCO - \langle\bigcirc\rangle - CO\right]_m$$

soft segment   hard segment

The poly(1,4-butylene ether glycol) has a molecular mass of between 1000 and 2000.

The morphology of these copolyether polyesters has been studied[5,6] and it has been concluded that the hard segments form crystalline lamellar domains, interspersed with amorphous material consisting of the soft segments and non-crystallised hard segments. The content of soft segment, as related to the hard segment, has a decisive influence on mechanical properties such as tensile strength and elongation as well as on the melting point of the copolyether polyesters[5].

The aim of this work has been to develop a method of analysing the copolyether polyesters, which is able to differentiate between the butanediol originating from the butanediol terephthalate hared segment and the butanediol from the polybutylene ether glycol terephthalate soft segment.

The cleavage of polyesters by chemical degradation has been reviewed recently[7]. Among the methods described, transesterification appears to be the most expedient, especially since it yields the carboxylic ester, which is easily determined by gas chromatography (GC), in a single step.

Transesterification of polyesters has been performed by refluxing a sample with lithium methoxide[8], with sodium methoxide in methanol[9] or with sodium methoxide, methyl acetate and methanol[10]. Interesterification of polyesters, with an excess of methyl acetate and sodium methoxide catalyst at 175°C and approximately 2.5 MPa pressure, was used to obtain methyl carboxylates and polyalcohol acetates[11].

In the present work it was found that pyrolysis–gas chromatography (Py–GC) is very useful for preliminary identification of the copolyether polyester and especially for differentiation between the copolyether polyester and poly(1,4-butanediol terephthalate) which may be considered as a copolyether polyester with 100 per cent hard segment component ($n = 0$). Interestification was not used, not only because by this method it would have been difficult to differentiate between the butanediol and the polybutylene ether glycol, but also in order to avoid working at high pressure.

In the transesterification step, diethyl terephthalate (DETP), 1,4-butanediol and poly(1,4-butylene ether glycol) (PBEG) are formed. DETP is determined on GC as such, while 1,4-butanediol is acetylated with acetic anhydride to give 1,4-butanediol diacetate (BDDA).

PBEG could not be acetylated with acetic anhydride. Using a method for the acetylation of ether linkages proposed by Karger and Mazur[12], and adapted to polyesters by Tsuji and Konishi[13], the PBEG was successfully acetylated. This method uses a mixture of p-toluene sulphonic acid and acetic anhydride as acetylating agents.

EXPERIMENTAL

Materials

The copolyether polyesters, containing varying ratios of hard (1,4-butanediol terephthalate) and soft (polybutylene ether glycol terephthalate) components were obtained from Du Pont (with the trade name "Hytrel") and from Akzo (with the trade name "Arnitel"). The poly(1,4-butanediol terephthalate) was supplied by Polysciences. Polybutylene ether glycol, with a molecular mass of 1000 (with the trade name "Terathane") was obtained from Du Pont. Reagent grade p-toluene sulphonic acid monohydrate and acetic anhydride were obtained from Merck. Diethyltereph-thalate (DETP) was prepared by reacting terephthaloyl chloride (Fluka) with so-

dium ethoxide, followed by the addition of water and subsequent extraction with methylene chloride. 1,4-Butanediol diacetate (BDDA) was prepared by refluxing 1,4-butanediol with acetic anhydride, followed by neutralisation and extraction with methylene chloride. Both DETP and BDDA were used to determine GC retention times and for calibration. The biphenyl used as an internal standard in the GC determination was obtained from BDH.

Instrumentation
      A dual-column Pye-Unicam Series 204 gas chromatograph was used with flame ionisation detectors.
      For Py–GC, a Pye-Unicam Curie point pyrolyser mounted on the injector of the gas chromatograph, was used. An iron wire, giving a temperature of 770°C at the Curie point, was used for pyrolysis. The method of hooking 200–300 μg of solid polymer onto the wire has been described[14]. A Carbowax 20M stationary phase was used to obtain the pyrograms. The operating conditions of the gas chromatograph are given in Table I.
      Milling of the polymers was carried out in a Wiley mill (Arthur Thomas) to particles of less than 0.5 mm diameter.

TABLE I

GAS CHROMATOGRAPHIC CONDITIONS

	Column packing	
	5% OV-225 on Chromosorb 100–120	*10% Carbowax 20M on Chromosorb W(80–100)**
Column (glass)	1.5 m × 0.4 mm I.D.	2.1 m × 0.4 mm I.D.
Injector temp. (°C)	250	125
Detector temp. (°C)	300	200
Nitrogen flow-rate (ml/min)	60	30
Temperature programme	150–250°C at 12°C/min	70°C for 10 min, 70–180°C at 16°C/min

      * Used in Py-GC.

Separation procedure by transesterification and acetylation reactions
      Into a 100-ml round bottomed flask with reflux condenser, 200 mg of copolyether polyester is introduced. After the addition of both 25 ml of 1 M sodium ethoxide solution in ethanol and 25 ml of ethyl acetate, the mixture is refluxed for 30 min. After cooling to room temperature, 50 ml of water is added and the mixture transferred to a 250-ml separation funnel where it is extracted with two portions of 50 ml of methylene chloride.
      The aqueous phase is concentrated, in a beaker, to a volume of about 20 ml. It is then transferred to a 50-ml round bottomed flask in which it is further concentrated to a dense slurry, to which 20 ml acetic anhydride is added. The mixture is refluxed for 1 h, cooled and brought to a pH of 6, with 10% sodium hydroxide solution. Then it is extracted with two portions of 25 ml methylene chloride. The methylene chloride solution is concentrated to 5 ml, then 10 mg accurately weighed

biphenyl internal standard is added and 1 μl of this solution is injected in the gas chromatograph to determine the 1,4-butanediol diacetate resulting from the 1,4-butanediol terephthalate hard segment.

The organic phase is concentrated to a volume of about 10 ml and transferred to a 25-ml round bottomed flask in which the rest of the solvent is evaporated. To the remaining precipitate 2 g of p-toluene sulphonic acid monohydrate, followed by 2 ml acetic anhydride, is added. The mixture is immediately heated and refluxed for 30 min. After cooling, 5 ml of water is added, the mixture is neutralised to a pH of between 6 and 7 and then extracted with two 25-ml portions of methylene chloride.

The organic phase is concentrated to 5 ml, then 20 mg accurately weighed biphenyl internal standard is added and 1 μl of this solution is injected in the GC (OV-225 column packing), for the determination of the diethylterephthalate and the 1,4-butanediol diacetate resulting from the polybutylene ether glycol terephthalate soft segment.

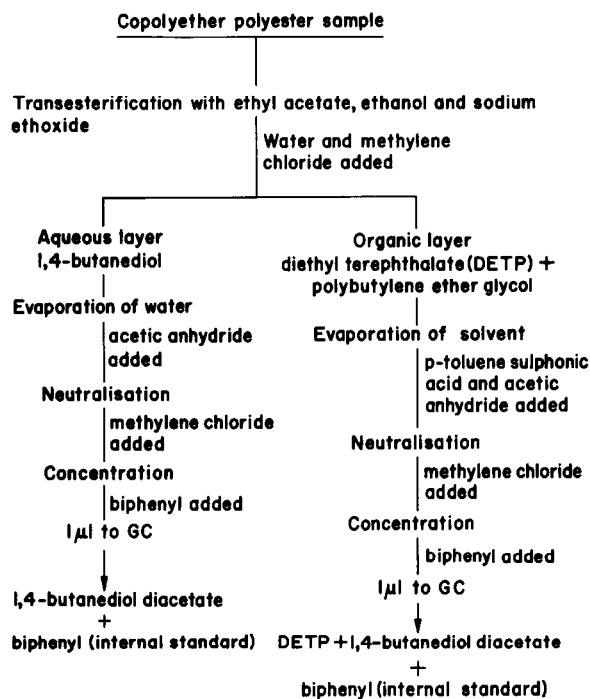A schematic illustration of the separation procedure is given in Fig. 1.

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                      Copolyether polyester sample
                                    |
                                    |
Transesterification with ethyl acetate, ethanol and sodium
ethoxide
                              | Water and methylene
                              | chloride added
              _____|_____
             |                                      |
      Aqueous layer                          Organic layer
      1,4-butanediol                  diethyl terephthalate(DETP) +
             |                            polybutylene ether glycol
Evaporation of water                              |
         | acetic anhydride           Evaporation of solvent
         | added                               | p-toluene sulphonic
Neutralisation                                  | acid and acetic
         | methylene chloride                   | anhydride added
         | added                        Neutralisation
Concentration                                   | methylene chloride
         | biphenyl added                       | added
   1 μl to GC                          Concentration
         |                                      | biphenyl added
         |                               1 μl to GC
         ↓                                      |
1,4-butanediol diacetate                        ↓
         +                      DETP + 1,4-butanediol diacetate
biphenyl (internal standard)                    +
                                 biphenyl (internal standard)
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Fig. 1. Diagram showing the course of separation.

RESULTS AND DISCUSSION

Identification by pyrolysis–gas chromatography

Py–GC offers an excellent way to identify the copolyether polyester rapidly, and especially to differentiate it from a pure poly(1,4-butanediol terephthalate) (PBTP). The pyrogram of PBTP is given in Fig. 2 and that of a copolyether polyester

in Fig. 3. On pyrolysis PBTP gives two prominent peaks: tetrahydrofuran (THF), resulting from the 1,4-butylene dioxy part and benzene which results from the terephthaloyl component. It is interesting to note that in a study on the Py–GC of PBTP, THF was not detected[15]. In the pyrogram of the copolyether polyester (Fig. 3) the benzene peak is less than a tenth as high as the THF. The ratios of the benzene to the THF peak in the pyrograms are for PBTP 5:10 and for copolyether polyesters < 1:10. The ratios given are the averages of more than ten determinations.
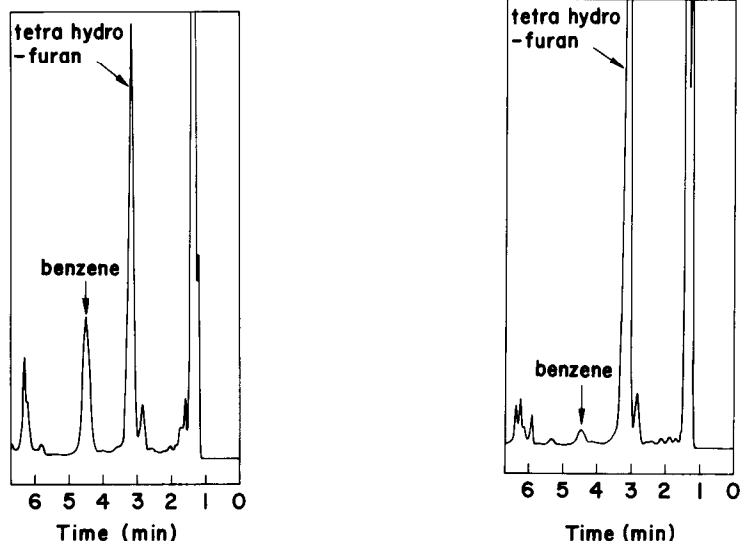
Fig. 2. Pyrogram of poly(1,4-butanediol terephthalate). Carbowax 20M column packing.

Fig. 3. Pyrogram of a copolyether polyester. Carbowax 20M column packing.

The reason for the great increase in the area of the THF peak in the pyrogram of the copolyether polyester is the presence in the latter of the polybutylene ether soft segment which, on pyrolysis, generates this increase in THF. The pyrogram of the polybutylene ether glycol (Terathane 1000), recorded similarly on the Carbowax 20M column packing, features THF as the main peak, while benzene does not appear at all.

GC separations

The GC separations are performed as the final steps of the wet chemical separations (see Experimental section and Fig. 1). In order to quantify the results, biphenyl was weighed and added to the final solution, to be injected in the gas chromatograph, to act as an internal standard. The analysis of BDDA, DETP and biphenyl on the OV-225 column packing (Fig. 4) gives well separated peaks. Calibration mixtures made up with the three pure compounds showed good reproducibility.

The transesterification step

The yield of the transesterification reaction with ethyl acetate, sodium ethoxide
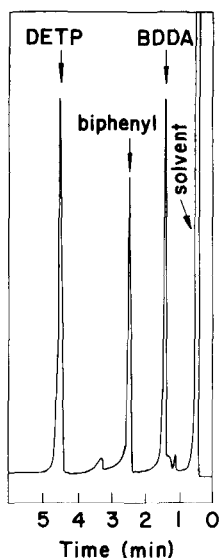
Fig. 4. Gas chromatogram showing separation of 1,4-butanediol diacetate (BDDA), biphenyl and diethyl terephthalate (DETP). For conditions see text.

and ethanol (as described in the Experimental section), was tested on poly(1,4-butanediol terephthalate) (PBTP) samples, both in pellet form and milled. The result obtained with diethyl terephthalate was multiplied by a factor obtained in the following way:

$$-CO-\langle\bigcirc\rangle-CO- \ / \ DETP \ = \ 132/222 = 0.59$$

Thus, the yield for milled PBTP expressed in terephthaloyl was 85% (mean of 12 experiments). It was found that unmilled PBTP samples (in pellet form) gave a 25% lower yield. The optimum reaction time was 30 min.

The terephthaloyl yield represents the total amount present, both in the hard as well as in the soft segments.

The 1,4-butanediol (or its sodium salt) formed in the transesterification step was then acetylated with acetic anhydride. It is interesting to note that 1,4-butanediol diacetate could be found in the transesterification mixture after refluxing but in very low quantities (2–3% of the theoretically possible). This suggests that the interesterification reaction which is quantitative at 175°C and high pressure[11] is beginning even under the mild conditions used in this work.

The result of the acetylation, which was obtained in 1,4-butanediol diacetate, was recalculated by multiplying by $-O-(CH_2)_4-O-$/BDDA = 88/174 = 0.51 to quantify the 1,4-butanedioxy part of the polymer.

The recovery rate of this part of the hard segment was about 25%. The much lower recovery obtained for the butanedioxy part, compared with the terephthaloyl part, may be explained by the dehydration of the glycol to give THF, which process

is known to take place under acidic conditions[16]. This side-reaction may compete with the main acetylation reaction, thus reducing the yield of the BDDA.

Acetylation of the polyether

The yield of the polyether acetylation was tested on a commercial poly(1,4-butylene ether glycol) (PBEG) (Terathane 1000). Attempts to perform the cleavage and acetylation of the PBEG with an excess of acetic anhydride under reflux failed, whereas reacting PBEG with a mixture of *p*-toluene sulphonic acid and acetic anhydride, as described in the Experimental section, gave significant amounts of BDDA after just a few minutes of heating under reflux. Shortly after the refluxing begins, the reaction mixture turns a dark brown colour. This suggests that side-reactions occur, reducing the yield of acetylation. THF formation was also observed by injecting the methylene chloride phase after acetylation and extraction, on a Carbowax 20M GC-column, under the conditions at which Py–GC was performed (Table I). The THF formed was found to be between 15 and 20% of the BDDA obtained.

The result of the polyether acetylation, obtained initially in 1,4-butanediol diacetate, was recalculated by multiplication by $-(CH_2)_4$-O-/BDDA $= 72/174 =$ 0.41. The recovery of the polyether building block, expressed as *n*-butaneoxy, was 45%.

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