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Determination of Carboxyl Endgroups and Comonomers in Poly(ethylene Terephthalate) with Hydrazine*

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Synopsis

On complete hydrazinolysis of poly(ethylene terephthalate), terephthalomonohydrazide is formed from carboxyl-end terephthaloyl residues in a quantity equivalent to the content of carboxyl endgroups in the polymer. The compound is separated from the reaction mixture by ion exchange and determined photometrically [ϵ_{240} in 0.1N HCl = 16,700 (1000 cm²/mole)]. A COOH determination carried out in this way is endgroup specific and, unlike titration, is not subject to interference by ionogenic fiber additives. Aromatic comonomers with acidic substituents (e.g., 5-sulfoisophthalic acid) in chemically modified, cationically dyeable poly(ethylene terephthalate) are determined simultaneously with the carboxyl endgroups by the same analytical method. In this case, the terephthalomonohydrazide and 5-sulfoisophthalodihydrazide are separated by ion exchange, and the difference in their spectral behavior is used for quantitative determination with the aid of a two-component analysis:

$$c_1 = (6.21\ D_{240} - 1.04\ D_{212}) \times 10^{-5} \text{ mole/l.}$$

$$c_2 = (2.62\ D_{212} - 0.51\ D_{240}) \times 10^{-5} \text{ mole/l.}$$

where c_1, c_2 = concentration of terephthalomonohydrazide and 5-sulfoisophthalodihydrazide, respectively; and D_{240}, D_{212} = optical density at 240 and 212 nm, respectively. The content of carboxyl endgroups in polyether esters poly(*p*-(2-ethyleneoxy)-benzoate), is determined on the basis of the *p*-(β-hydroxyethoxy)benzoic acid [ϵ_{258} in 0.1N HCl = 16,100 (1000 cm²/mole)] liberated from carboxyl-end monomer units by hydrazinolysis. For copolyether esters with *p*-(β-hydroxyethoxy)benzoic acid as a comonomer, the contents of carboxyl-end terephthalic acid and p-(β-hydroxyethoxy)-benzoic acid are determined simultaneously with the aid of a spectrophotometric two-component analysis:

$$c_1 = (7.65\ D_{240} - 3.27\ D_{258}) \times 10^{-5} \text{ mole/l.}$$

$$c_2 = (7.91\ D_{258} - 3.49\ D_{240}) \times 10^{-5} \text{ mole/l.}$$

where c_1, c_2 = concentration of terephthalomonohydrazide and p-(β-hydroxyethoxy)-benzoic acid, respectively; and D_{240}, D_{258} = optical density at 240 and 258 nm, respectively.

INTRODUCTION

In addition to the specific hydroxyl endgroups resulting from its synthesis, every poly(ethylene terephthalate) (PET) also contains carboxyl end-

* Dedicated to Prof. Dr.-Ing. Habil. Clemens Sustmann on the occasion of his seventieth birthday.

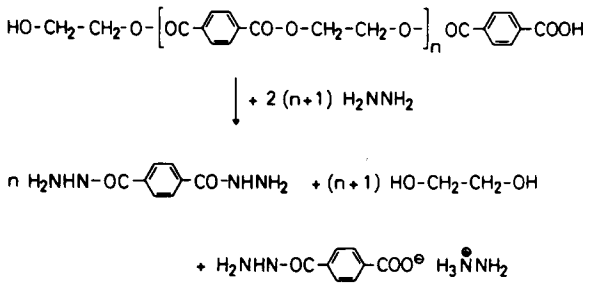


Fig. 1. Reaction of poly(ethylene terephthalate) with hydrazine.

groups. These are due to thermal cleavage of the polymer chains because of the long residence times and relatively high polycondensation temperatures required to reach high molecular weights.[1-3] The ratio of hydroxyl to carboxyl groups provides a basis for assessing the chemical quality of the polyester.[4] The content of carboxyl groups is particularly important, since it is a significant factor in connection with the polymer's sensitivity to hydrolysis,[5] in which these endgroups have a catalytic effect.[6] Their number can be increased not only by hydrolysis but also by photolytic damage and thermal oxidation.[7-11]

The main analytic method for the carboxyl groups in PET is acidimetric titration, the endpoint being determined visually[12] or photometrically[13] with the addition of an indicator, potentiometrically,[14] or conductimetrically.[15] Chemical methods developed for the determination of carboxyl endgroups in aliphatic polyesters[16,17] have not found any application for PET.

A new possibility for the chemical determination of carboxyl endgroups in PET is offered by the application of the principle developed by Akabori et al.[18] for the determination of C-terminal amino acids in proteins.[19] The readily occurring hydrazinolytic degradation of PET (Fig. 1) has been used for a wide variety of purposes, e.g., for the separation of PET from blends with wool,[20] the investigation of the harmful action of organic bases on PET fibers,[21] the determination of the degree of crosslinking of cured polyester resins,[22] and the determination of the contents of methyl ester and diethylene glycol groupings in PET.[4,23,24] However, no analytic use has yet been made of the fact that the carboxyl groups of terminal terephthalic acid in the polymer molecule are unchanged in the reaction with hydrazine, and terephthalomonohydrazide is liberated from these C-terminal terephthaloyl residues in a quantity equivalent to the quantity of carboxyl groups present in the polymer. The quantitative determination of this compound thus provides a method based on hydrazinolysis for the determination of carboxyl endgroups in PET.

The terephthalomonohydrazide, which is formed in very small quantities corresponding to the low absolute content of carboxyl endgroups in the normal fiber polymer (10–50 meq/kg[25]), cannot be determined in the reaction mixture in the presence of the main product, terephthalodihydrazide.

Concentration of the monohydrazide is therefore necessary for its quantitative determination; this can be achieved by ion exchange on the free carboxyl group. The COOH determination method based on hydrazinolytic degradation thus involves the following steps: (1) hydrazinolysis of the polyethylene terephthalate; (2) isolation of the terephthalomonohydrazide; (3) quantitative determination of the terephthalomonohydrazide.

EXPERIMENTAL

Materials and Apparatus

Polyester fibers and fabrics are extracted with petroleum ether (40–80°C) for 12 hr in a Soxhlet apparatus and dried for 6 hr at 60°C under vacuum (12 mm Hg). Polyester chips with a water content of 0.06% to 0.17% are analyzed without pretreatment.

The following substances are used for the COOH determination: dioxane (distilled twice over sodium: $\leqslant 10$ ppm H_2O); *n*-butanol (distilled and dried over 4-Å molecular sieve: 50 ppm H_2O); anhydrous hydrazine (C. Roth, Karlsruhe); QAE-Sephadex A-25 ion exchanger (Pharmacia, Uppsala, Sweden); 0.1*N* HCl Titrisol (E. Merck, Darmstadt).

The ion exchange is carried out in a Merrifield apparatus (Fig. 2). The dimensions of the apparatus must be the same in every case. The factor

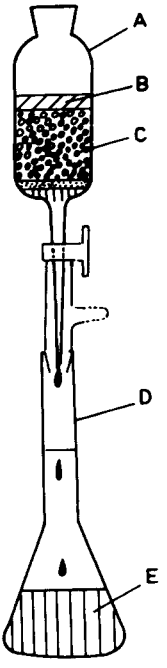


Fig. 2. Ion exchange procedure for terephthalomonohydrazide: (A) Merrifield apparatus; (B) 0.1*N* HCl; (C) QAE-Sephadex A-25; (D) 100-ml volumetric flask; (E) ion exchange eluate.

by which the 0.1*N* HCl used for elution is diluted by the water present in the swollen ion exchanger and in the free space of the apparatus is determined by titration. Hydrochloric acid of the normality found in this way is used as a reference solution for the photometric measurements on the ion exchange eluates.

For characterization of the terephthalic and isophthalic acid derivatives, which have very high melting points and melt with decomposition, the endothermic melting peak is determined with a differential thermal analyzer, Model du Pont 900 (heating rate, 15°C/min; final temperature, 450°C; atmosphere, nitrogen). The ΔT values corresponding to the melting points are underlined.

Procedure for Determination of Carboxyl Groups

Polyester fibers, 0.100 g, are weighed on an analytical balance into a 50-ml pear-shaped flask, 25 ml of a 15% hydrazine solution in dioxane/*n*-butanol (70:15) is added, and the mixture is allowed to react for 5 hr at 70°C in a constant-temperature bath with occasional shaking. The flask is tightly closed with a polyethylene stopper, but this is opened for a short time at the start of heating (50°C) to reduce the excess pressure produced. For the investigation of polyester chips (0.100–0.150 g), the latter are shaken mechanically with 25 ml of a 35% hydrazine solution in dioxane/*n*-butanol (53:12) for 10 hr at room temperature.

The reaction solution is evaporated and the residue is dried for 4 hr over concentrated H_2SO_4 under vacuum (1.0–0.5 mm Hg). The residue is digested in portions with a total of 15 ml water, and the resulting suspension is centrifuged for 30 min at 4400 rpm. The precipitate is washed twice with 2.5-ml portions of water and centrifuged. The combined supernatants are introduced into 2.0 g QAE-Sephadex A-25 ion exchanger equilibrated with water in a 40-ml Merrifield apparatus (Fig. 2).

After an adsorption time of 12 hr with occasional shaking, 700 ml water is passed through the ion exchanger, which is then eluted directly into a 100-ml graduated flask with 0.1*N* hydrochloric acid until the liquid reaches the 100-ml mark. Photometry is then carried out on the eluate at 240 nm against hydrochloric acid (as described above).

Syntheses

Terephthalomonohydrazide. With stirring and cooling in CO_2/acetone, 9.0 g (0.05 mole) of monomethyl terephthalate (Th. Schuchardt, Munich) is added to a solution of 24.0 g (0.75 mole) anhydrous hydrazine in 5 ml absolute methanol. The mixture is warmed to room temperature, stirred for 48 hr, and evaporated. The reaction product is taken up in 130 ml water and converted into the free acid by a batch-type ion exchange treatment (160 g Dowex Type 1 × 2, Serva, Heidelberg; total capacity, 3.64 meq/g; adsorption time, 10 hr). Water, 2 liters, is passed through the resin, which is then digested with 200 ml 6*N* acetic acid. The terephthalomonohydrazide precipitates finely dispersed and is separated by filtering off

the resin through a sintered glass filter. It is freed from acetic acid by repeated digestion in boiling water and evaporation, and recrystallized once from water and twice from methanol. Yield, 5.9 g (61.5% theoretical yield), ΔT(endo): 236°C (lit.[26] >250°); (sublimation >224°C; ΔT-(endo): 376°, 415°).

ANAL. Calcd for $C_8H_8N_2O_3$ (180.17): C, 53.33%; H, 4.48%; N, 15.55%. Found: C, 53.09%; H, 4.37%; N, 15.42%.

Hydrazinium (Monohydrazido)terephthalate. The mixture is prepared as above. The reaction solution is filtered and 250 ml absolute methanol is added. The precipitate formed is filtered off and thoroughly washed with methanol. Yield, 5.9 g (55.6% theoretical yield); ΔT(endo): 160°C, 182°, 193°, 236°, 393°.

ANAL. Calcd for $C_8H_{12}N_4O_3$ (212.22): C, 45.28%; H, 5.70%; N, 26.40%. Found: C, 45.76%; H, 5.39%; N, 26.39%.

Hydrazinium Bis(monohydrazido)terephthalate. The mixture is prepared as above. The evaporation residue is repeatedly digested in water and reevaporated. The product is recrystallized twice from the smallest possible quantity of water. Yield, 5.05 g (51.0% theoretical yield); ΔT-(endo): 235°C, 392° (sublimation >178°).

ANAL. Calcd for $C_{16}H_{20}N_6O_6$ (392.38): C, 48.97%; H, 5.14%; N, 21.42%; O, 24.45%. Found: C, 48.97%; H, 5.05%; N, 21.41%; O, 24.53%.

Terephthalomonohydrazide Hydrochloride. Terephthalomonohydrazide, 0.09 g (5×10^{-4} mole), is dissolved in a solution of 7.5 ml (7.5×10^{-4} mole) 0.1*N* hydrochloric acid in 25 ml methanol. The solution is evaporated to dryness and the product is dried over potassium hydroxide. Yield, 0.11 g (100% theoretical yield).

ANAL. Calcd for $C_8H_9N_2O_3Cl$ (216.63): C, 44.36%; H, 4.19%; N, 12.93%; Cl, 16.37%. Found: C, 44.20%; H, 4.72%; N, 12.81%; Cl, 16.26%.

Isophthalodihydrazide 5-Sodium Sulfonate. With stirring and cooling in CO_2/acetone, 14.8 g (0.05 mole) dimethyl isophthalate 5-sodium sulfonate (Rhône-Poulenc-Textile, Lyon) is added to a solution of 48.0 g (1.5 mole) anhydrous hydrazine in 30 ml absolute methanol. After warming to room temperature, the mixture is stirred for 60 hr, and methanol is added to the resulting suspension until no further precipitate separates. The precipitate is filtered off and extracted with boiling methanol. Yield, 10.5 g (77.0% theoretical yield); ΔT(endo): 328°C.

ANAL. Calcd for $C_8H_9N_4NaO_5S$ (296.25): C, 32.43%; H, 3.06%; N, 18.91%; Na, 7.76%; S, 10.83%. Found: C, 32.47%; H, 3.30%; N, 18.90%; Na, 7.45%; S, 11.30%.

***p*-(β-Hydroxyethoxy)benzoic Acid.** Preparation by the method of Kuriyama et al.[27]; the product is recrystallized twice from water; mp, 189°C (lit. 179°C).

ANAL. Calcd for $C_9H_{12}O_4$ (182.40): C, 59.30%; H, 5.49%; O, 35.14%. Found: C, 59.28%; H, 5.65%; O, 35.18%.

RESULTS AND DISCUSSION

Hydrazinolysis of Poly(ethylene Terephthalate)

Determination of Uniformity of the Reaction

The determination of carboxyl endgroups by the method described is possible only if the hydrazinolysis of the ester linkages proceeds quantitatively and does not lead to any other terephthalic acid derivatives apart from terephthalodihydrazide and terephthalomonohydrazide.

It is known that in the preparation of low molecular weight acid hydrazides at high temperatures and with a small molar excess of hydrazine, secondary hydrazides may be formed, with loss of hydrazine, as by-products[28]:

$$2\ R{-}CO{-}NHNH_2 \rightarrow R{-}CO{-}NHNH{-}OC{-}R + H_2NNH_2$$

To avoid this possible side reaction,[29] a large excess of hydrazine is used (N_2H_4:PET = 38–53:1 w/w), and the reaction is carried out at 25°, 50°, and 70°C.

To check the uniformity of the reaction, the following investigations were carried out on Terylene W16 and Trevira 220. (a) On thin-layer chromatography of the hydrazinolysis product, two spots can be detected with fluorescence indicator or picryl chloride; these spots correspond to the reference substances terephthalomonohydrazide and terephthalodihydrazide (Fig. 3). (b) After evaporation of the hydrazinolysis product to dryness and extraction with water to remove terephthalomonohydrazide, the result of an elemental analysis corresponds to that of terephthalodihydrazide. (c) The hydrochloric acid ion exchange eluate of the aqueous extract from the hydrazinolysis product gives a UV spectrum identical with that of terephthalomonohydrazide in 0.1*N* HCl (Fig. 4). (d) In a concentrated ion exchange eluate, thin-layer chromatography shows only one substance

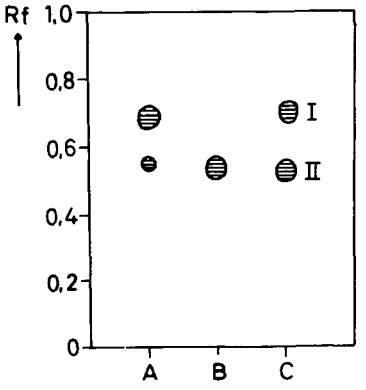


Fig. 3. Thin-layer chromatogram of the hydrazinolysis product of a poly(ethylene terephthalate): (A) before ion exchange; (B) after ion exchange; (C) reference substances (I = terephthalodihydrazide, II = terephthalomonohydrazide). Silicagel HF 254; dioxane/ammonia (25%)/water = 65/8/27.

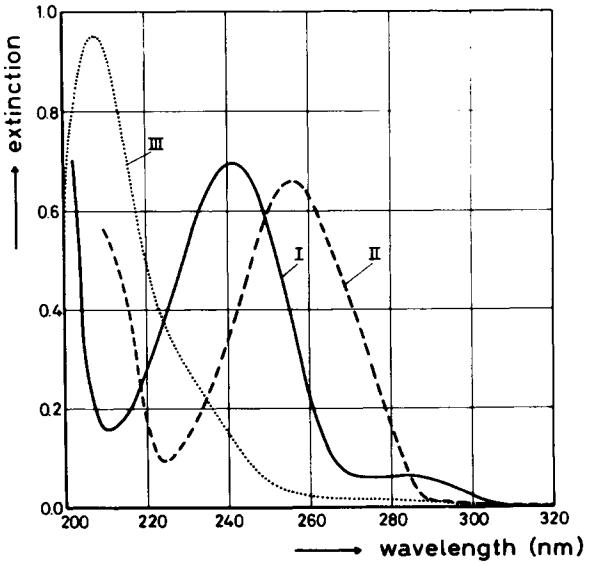


Fig. 4. UV spectra (in 0.1*N* HCl) of terephthalomonohydrazide (I), *p*-(β-hydroxyethoxy)benzoic acid (II): $c = 4 \times 10^{-5}$ mole/l., and isophthalodihydrazide 5-sodium sulfonate: $c = 2 \times 10^{-5}$ mole/l.

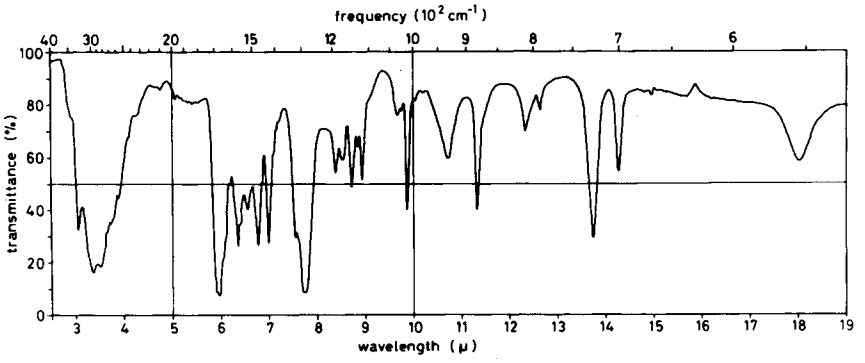


Fig. 5. IR spectrum of terephthalomonohydrazide hydrochloride.

whose R_f value agrees with that of terephthalomonohydrazide (Fig. 3). (e) The residue obtained on evaporation of an ion exchange eluate prepared with 0.1*N* HCl has an IR spectrum that corresponds to that of terephthalomonohydrazide hydrochloride (Fig. 5).

The reaction mixture from the hydrazinolysis of PET thus contains no terephthalic acid derivatives other than terephthalodihydrazide and terephthalomonohydrazide.

Dependence on Time and Temperature

The rate of degradation of PET with hydrazine or hydrazine hydrate as a function of the reaction temperature and the reagent concentration has

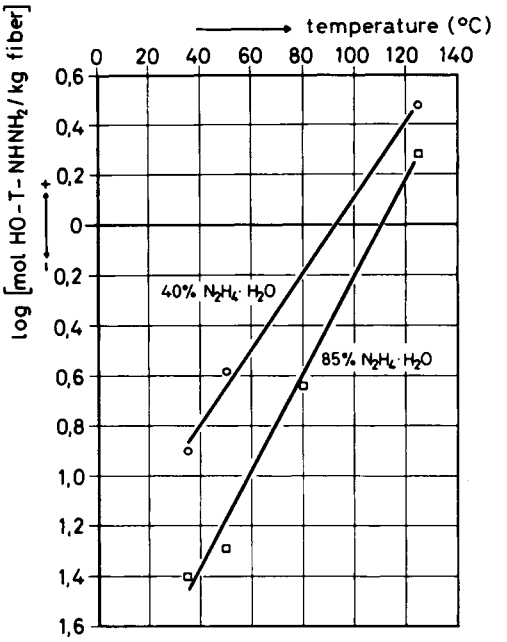


Fig. 6. Formation of terephthalomonohydrazide (HO-T-NHNH$_2$) during the reaction of Terylene W16 with hydrazine hydrate as a function of temperature.

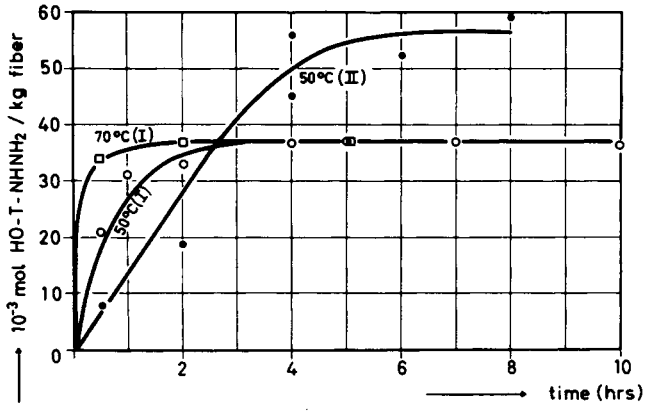


Fig. 7. Formation of terephthalomonohydrazide (HO-T-NHNH$_2$) as a function of time and temperature during the reaction of Terylene W16 with hydrazine: (I) 15% in dioxane/*n*-butanol, 70/15; (II) 15% in *n*-butanol.

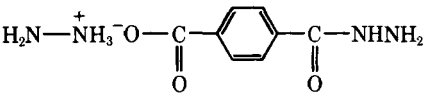
been investigated by several authors[4,20,21,23,24]. In these investigations, strength measurements[20,21] or gravimetric determination of unreacted polyester material[23] were used to follow the course of the reaction. Chemical determination of the progressive cleavage of the ester groups has not so far been used. However, this is possible by measurement of the terephthalomonohydrazide formation.

In the reaction of PET with hydrazine hydrate, the formation of terephthalomonohydrazide increases exponentially with the reaction temperature; this is due to base-catalyzed ester hydrolysis in competition with the hydrazide formation. The water present in the reaction mixture liberates carboxyl groups, with the result that the quantity of terephthalomonohydrazide formed is greater than that corresponding to C-terminal terephthaloyl residues (Fig. 6). Anhydrous hydrazine must therefore be used for a carboxyl endgroup determination based on hydrazinolysis. To facilitate handling, the hydrazine is diluted with organic solvents for the reaction with PET.

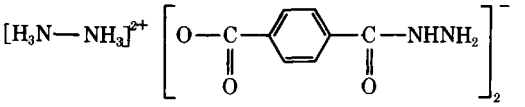
Hydrazine dissolves readily in alcohols, but these solvents competitively inhibit its reactivity because of complex formation.[20] This is confirmed by a comparison of the time dependence of the terephthalomonohydrazide formation in butanolic hydrazine (15%) and in a mixture of hydrazine (15%) with dioxane/*n*-butanol (70:15), in which the alcohol acts as a solubilizing agent (Fig. 7).

Isolation of Terephthalomonohydrazide

Solubility of Terephthalohydrazides. Terephthalomonohydrazide can be readily extracted from the evaporated hydrazinolysis product with water, particularly since the compound is present in the reaction mixture as the readily soluble hydrazinium (monohydrazido)terephthalate[30]:



This is also obtained from monomethyl terephthalate by reaction with hydrazine and precipitation of the reaction product with methanol. Recrystallization of this product from a very small quantity of water yields hydrazinium bis(monohydrazido)terephthalate:



A simple separation of the hydrazinium (monohydrazido)terephthalate from the hydrazinolysis product purely on the basis of its solubility is impossible, since it can be shown by thin-layer chromatography and by electrophoresis that terephthalodihydrazide, which is present in a large excess in the hydrazinolysis product, dissolves in traces despite its low solubility (Table I). An ion exchange method is therefore the only possibility for a quantitative separation of the terephthalomonohydrazide.

Ion Exchange in the Batch Method. Since only one component is to be isolated in the present separation problem, it is advantageous to carry out the ion exchange by the fast batch process. Since it is possible to wait until equilibrium has been reached in the system and the component in question

TABLE I
Solubility of Terephthalohydrazides at 25° [a]

Compound	Solvent	Dissolved compound 10^{-4} mole/l.
Terephthalodihydrazide	H_2O	6
Terephthalomonohydrazide	H_2O	101
	0.1*N* HCl	400
Hydrazinium (monohydrazido)-terephthalate	H_2O	470

[a] Determined by measuring the O.D. at 240 nm.

has been completely bound under the prevailing reaction conditions, this method can be used for a quantitative separation.[31,32]

The aqueous suspension of the evaporated hydrazinolysis product is centrifuged to separate the delustering agent and undissolved terephthalodihydrazide, and the basic ion exchanger is then digested with the supernatant to adsorb the terephthalomonohydrazide. The hydrazine liberated from its salt and the traces of terephthalodihydrazide extracted at the same time are then washed out of the exchanger. Finally, the exchanger is digested with a desorbent, and the terephthalomonohydrazide is eluted in one elution step.

The use of polystyrene resin exchanger (Dowex Type 1 × 2) is found to be unsuitable for the present separation problem, since large quantities of substance cannot be desorbed owing to nonspecific adsorption. On the other hand, the strongly basic anion exchanger QAE-Sephadex A-25 does not exhibit nonspecific adsorption for aromatic compounds and is therefore well suited to the isolation of terephthalomonohydrazide.

QAE-Sephadex A-25, 0.36 g, (total capacity, 3.0 ± 0.4 meq/g) equilibrated in water at pH 5.8–5.9 is sufficient for the complete adsorption of 2.5 × 10^{-6} mole of terephthalomonohydrazide. The adsorption is independent of the pH of the original solution in the pH range of 5–7. Complete ionization of the weakly acidic carboxyl group of terephthalomonohydrazide (pK = 4.63), which is necessary for its bonding and would require a higher pH, is achieved by the strongly basic ion exchanger. An adsorption time of 3 hr is sufficient.

As Figure 8 shows, an ionic strength of 0.1 mole/l. is necessary for the quantitative desorption of 2.5 × 10^{-6} mole of terephthalomonohydrazide adsorbed on 2 g QAE-Sephadex A-25 with the small elution volume of 100 ml. The experiments were carried out with sodium chloride solution, though terephthalomonohydrazide has a lower extinction coefficient in this solution than with the protonated carboxyl group in hydrochloric acid solution (Table II). Since this is unfavorable for the subsequent photometric determination of the compound, 0.1*N* hydrochloric acid was given preference as the eluent for the analytic method. The dextran matrix of the exchanger is not degraded during the short elution time (20–30

TABLE II
Molar Extinction Coefficients (1000 × cm²/mole)

Compound	λ, nm	ε	Solvent
Terephthalomonohydrazide	258	7,400	0.1*N* HCl
	249	14,600	0.1*N* HCl
	242 (λ_{max})	16,800	0.1*N* HCl
	240	16,700	0.1*N* HCl
	212	3,300	0.1*N* HCl
	249 (λ_{max})	13,100	1.0*M* NaCl
Isophthalodihydrazide	240	6,700	0.1*N* HCl
5-sodium sulfonate	212	40,000	0.1*N* HCl
p-(β-Hydroxyethoxy)-	258 (λ_{max})	16,100	0.1*N* HCl
benzoic acid	240	7,900	0.1*N* HCl

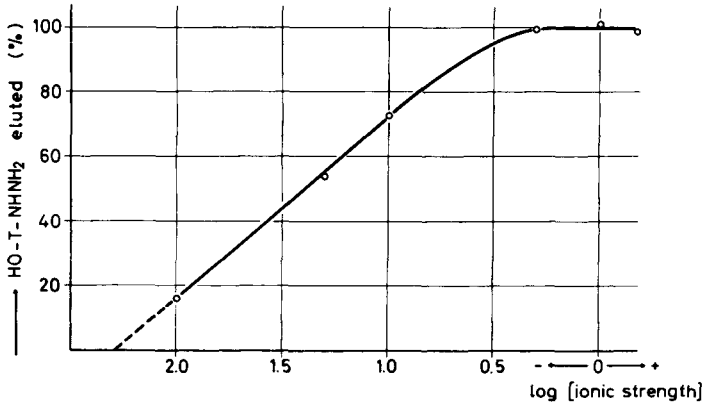


Fig. 8. Desorption of terephthalomonohydrazide (HO-T-$NHNH_2$, each essay 2.5 × 10^{-6} mole) from QAE-Sephadex A-25 as a function of ionic strength (aqueous NaCl, each essay 100 ml).

min), and the elution solutions consequently have no additional UV absorption due to degradation products.

Quantitative Determination of Terephthalomonohydrazide. As was shown by thin-layer chromatography, no aromatic compounds other than terephthalomonohydrazide are present in the ion exchange eluate of the PET hydrazinolysis product (Fig. 3). The compound can therefore be determined by UV spectroscopy in the elution solution itself (absorption maximum, 242 nm; Fig. 4, Table II).

The molar extinction coefficient of terephthalomonohydrazide at this wavelength is high enough to give a low detection limit. In sodium chloride solution, on the other hand, there is a displacement of the absorption maximum to 249 nm and a decrease in the molar extinction coefficient at this wavelength.

To construct a calibration line, a concentration series of terephthalomonohydrazide, (0.5–5.0) × 10^{-5} mole/l. of 0.1*N* HCl, was prepared and subjected to photometry at 240 nm. The Beer-Lambert law is obeyed, and the detection limit is 3 × 10^{-7} mole terephthalomonohydrazide/l.

TABLE III
Reproducibility of Carboxyl Endgroup Determination by Hydrazinolysis

Sample	Carboxyl endgroups, meq/kg			
	Average value[a] $\bar{x}$	Standard deviation s	Confidence interval[b] q	Coefficient of variation V, %
Tergal, 2.2 dtex/endl., semidull	25.4	2.4	2.0	9.6
Tergal, 4.4 dtex/endl., dull	25.5	2.4	2.0	9.5
Trevira tissue, 50 dtex, text., bright	14.9	1.5	1.2	9.9

[a] $N = 8$.
[b] For 95% statistical certainty.

Reproducibility of the Method

After determination of the optimum conditions for the analysis, eight determinations of the carboxyl group content were carried out on each of three PET materials. The results are as shown in Table III.

Application of Hydrazinolysis Method

Investigation of Commercial Poly(ethylene Terephthalate) Fibers

Various commercial PET fiber types were examined by the hydrazinolysis method. The results are shown in Table IV. Terylene W16 and Diolen FL are pilling-resistant fibers with low molecular weights; Trevira 550 and 560 are chemically modified high-shrinkage PET fibers. With the exception of the Tergal endless filaments, they are all staple fibers.

TABLE IV
Content of Carboxyl Endgroups in Commercial Poly(ethylene Terephthalate) Fibers

Trade name	Fineness/length, dtex/mm	COOH, meq/kg	
		Hydrazinolysis method	Colorimetric indicator method[a]
Terylene W11	4.4/90, bright	32	
Terylene W16	4.8/90, semidull	37	37
Diolen	4.6/90, bright	40	64
Diolen FL	5.0/60, bright	59	56
Trevira 220	4.8/60, bright	20	20
Trevira 220	4.5/60, dull	22	34
Trevira 550	3.9/90, dull	17	13
Trevira 560	3.2/120, dull	21	16
Tergal	2.2/endl., semidull	25	36
Tergal	4.4/endl., dull	26	35

[a] Reproducibility, q = 1.1–3.5 meq COOH/kg (for 95% statistical certainty); V = 2.2%–14.6%.

TABLE V
Content of Carboxyl Groups in Polyester Fabrics Set by Different Treatments (Trevira, Textured)

Sample	COOH, meq/kg	
	Hydrazinolysis method	Colorimetric indicator method
Untreated	14	46
Steamed (12 min, 120°, 1.4 atü)	15	42
Boiled (35 min, 0.1% Nekanil, $5 \times 10^{-3}M$ Na_2CO_3)	15	20

The results are compared with values obtained by a colorimetric indicator method. The principle of this method was used by Hensley[33] for the determination of traces of acid in dimethyl terephthalate. In the investigation of PET, the color reaction that occurs with the carboxyl groups on addition of the indicator bromophenol blue in its anionic form is used for the quantitative photometric determination of these groups. The decrease in blue color is proportional to the number of equivalents of acid present in the polymer.

The inadequacy of this nonspecific method can be seen on comparison of its results with those obtained by hydrazinolysis. The divergences, which are large in some cases, are due to the fact that the color change of the indicator can be influenced by ionogenic fiber additives, whereas these additives have no influence on the endgroup specific formation of terephthalomonohydrazide and its determination. Similar deviations are found in the amino endgroup determinations on nylon fibers by titration and by dinitrophenylation.[34–36] This is because titration methods are not endgroup specific and can give reasonably reliable results only for average molecular weights of up to 20,000. Above this limit, the ratio of endgroups (which are present in very low concentrations) to frequently undefinable impurities that interfere with the titration becomes increasingly unfavorable. This is a disadvantage that cannot be overcome by the use of larger samples of polymer and dilution of the titrant.[37]

The advantages of the chemical determination of endgroups by hydrazinolysis are also shown by investigations on polyester fabrics set by different treatments. The carboxyl endgroup values obtained by the indicator method show a decrease of about 100% after the boiling treatment required for setting, though this treatment can lead to an increase as a result of hydrolysis (Table V).

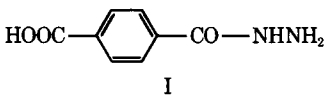
Investigation of Commercial Chemically Modified Polyester Fibers

Basically Dyeable Polyesters. The hydrazinolysis method is also suitable for the investigation of chemically modified polyesters; and, in addition to the determination of the carboxyl endgroup content, it allows the quantitative determination of aromatic comonomers with acidic substituents.

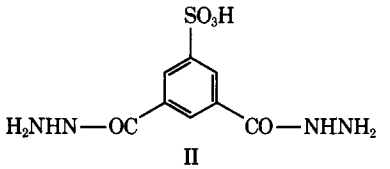
TABLE VI
Content of Carboxyl Endgroups
and of Comonomers in Copolyester and Homopolyester Fibers

Trade name	C-terminal Terephthalic acid, mmole/kg	C-terminal *p*-(β-Hydroxy-ethoxy)benzoic acid, mmole/kg	5-Sulfoiso-phthalic acid, mmole/kg
Dacron 64c	21	—	86
Dacron 65	35	—	94
Dacron 89	38	—	82
Unitika (copolyether ester)	29	8	—
Unitika A-Tell (homopolyether ester)	—	32	—

Thus, the ion exchange treatment of the hydrazinolysis product of basically dyeable polyester fibers, which are copolymerized with isophthalic acid 5-sodium sulfonate, results in the isolation not only of terephthalomonohydrazide but also of the hydrazides formed from the comonomer (owing to the unchanged sulfo group). The ion exchange eluate obtained may be regarded as a two-component system if no distinction is made between the sulfoisophthalic acid derivatives isolated together with the terephthalomonohydrazide. It thus becomes possible to carry out a simultaneous quantitative determination of the total comonomer content and of the carboxyl endgroups, which are equivalent to C-terminal terephthalic acid. Terephthalomonohydrazide (I) and 5-sulfoisophthalodihydrazide (II), are used as calibration substances for the development of a two-component analysis from the differences in the spectral behavior of the compounds (Table II):



I



II

$$c_1 = (6.21\ D_{240} - 1.04\ D_{212}) \times 10^{-5}\ \text{mole/l.}$$

$$c_2 = (2.62\ D_{212} - 0.51\ D_{240}) \times 10^{-5}\ \text{mole/l.}$$

where c_1, c_2 = concentration of terephthalomonohydrazide (I) and 5-sulfoisophthalodihydrazide (II), respectively; and D_{240}, D_{212} = optical density at 240 and 212 nm, respectively. Comonomer contents if 1.6 to 1.8 mole-% of isophthalic acid 5-sodium sulfonate, based on the monomer unit [OCH_2CH_2OOC-C_6H_4-CO], were found for three basically dyeable PET copolyester fibers (Table VI).

Polyether Esters. The ester linkages in homo- and copolyether ester fibers with *p*-(β-hydroxyethoxy)benzoic acid as a monomer or comonomer unit are also completely broken by hydrazine, though only after a fairly

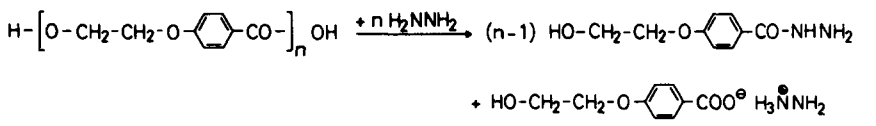


Fig. 9. Reaction of poly[*p*-(2-ethyleneoxy)benzoate] with hydrazine.

long reaction time (Fig. 9). In the case of poly[*p*-(2-ethyleneoxy)benzoate], *p*-(β-hydroxyethoxy)benzoic acid, which is equivalent to the C-terminal carboxyl groups of the polymer, is isolated by the hydrazinolysis method and determined quantitatively with the corresponding pure compound as the calibration substance (Table VI). On the other hand, terephthalomonohydrazide and *p*-(β-hydroxyethoxy)benzoic acid corresponding to the different C-terminal monomer units are isolated from the hydrazinolysis product of the copolyether ester. The number ratio of the monomer units carrying carboxyl groups can be determined on the basis of a two-component analysis developed with the pure compounds:

$$c_1 = (7.65\ D_{240} - 3.27\ D_{258}) \times 10^{-5}\ \text{mole/l.}$$

$$c_2 = (7.91\ D_{258} - 3.49\ D_{240}) \times 10^{-5}\ \text{mole/l.}$$

where c_1, c_2 = concentration of terephthalomonohydrazide and *p*-(β-hydroxyethoxy)benzoic acid, respectively; and D_{240}, D_{258} = optical density at 240 and 258 nm, respectively. This may be regarded as a first step toward a chemical sequence analysis of this polymer, which has already been attempted by high-resolution NMR spectroscopy.[38]

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