Quantitative Analysis of Copolyamides and Copolyesters by Gas Chromatography

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Synopsis

Procedures were developed for the analysis of copolyesters and copolyamides by saponification or hydrolysis of the copolymers to their component dicarboxylic acids, glycols, amino acids, or diamines and quantitatively identifying these by gas chromatography. The alcohols, amines and acids were converted to volatile trimethylsilyl derivatives for the analysis, and linear correlations were observed between carbon atom contents of these derivatives and retention times in the chromatograph.

INTRODUCTION

Gas chromatography (GC) coupled with controlled thermal degradation has found increasing use in the analysis of vinyl copolymers, particularly those that degrade to their original monomers or related oligomers.[1] Few reports, however, are found on the application of GC to the analysis of the degradation products of condensation or step-growth polymers, partly because of the low volatility of the initial monomers or degradation products, which are generally solid or high-boiling polar compounds with strong hydrogen bonding capability. This volatility problem has been overcome for such compounds by converting them to derivatives that are free of active hydrogen bonding sites, such as trimethylsilyl (TMS) derivatives as follows[2]:

$$MH + RSi(CH_3)_3 \rightarrow MSi(CH_3)_3 + RH$$

This technique has been applied in the present report to the analysis of copolyesters and copolyamides (and related homopolymers) by saponification and acid hydrolysis, respectively, of the copolymers to their monomeric precursors and conversion of these to trimethylsilyl derivatives. The reagent used for the latter reaction was N,O-bis(trimethylsilyl)acetamide (BSA), which has the ability to replace an active hydrogen with a TMS group.[3]

In order to develop a quantitative analysis procedure by GC it was necessary to first ascertain the number of TMS groups added to each monomer. Most of the work reported in the literature has dealt with amino acids derived from protein hydrolysis, and it has been demonstrated that for glycine, for example, the formation of the tris-TMS derivative is favored by the use of polar solvents such as acetonitrile.[4] Analogous information is not available for the diamines and diacids found in common nylon homopolymers and copolymers, so initial studies were directed to this end.

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RESULTS

Determination of Copolyamide Composition

The trimethylsilylation of polyamide hydrolyzates should be analogous to that of glycine; so to verify the extent of silylation in these products, several diamines and diacids were reacted with BSA in acetonitrile and chromatographed. For hexamethylenediamine as an example, the addition of at least one TMS group was verified by the decreased retention time of this compound in the GC analysis; and for the diacids the appearance of GC peaks in their reaction products with TMS indicated the success of this approach because they were too nonvolatile to be chromatographed before this reaction. For more quantitative information the extent of substitution was determined by hydrolyzing, trimethylsilylating, and chromatographing nylon 66. Peak areas were measured and mole percents of hexamethylenediamine (HMDA) and adipic acid were calculated (based on the equation in Table I) for all possible combinations of TMS groups, with the results listed in Table I.

The data in Table I were obtained by assuming that the peak area ratios are equal to the weight ratios of the components. The components, in turn, may be either mono- or bis-TMS derivatives of the diacid and either mono-, bis-, tris-, or tetrakis-TMS derivatives of the diamine. From the molecular weights of each of the possible derivatives and the peak areas, the possible mole ratios were calculated and converted to mole percent in Table I. Nylon 66 should of course contain 50 mole-% HMDA, and the data in Table I show that the only combi-

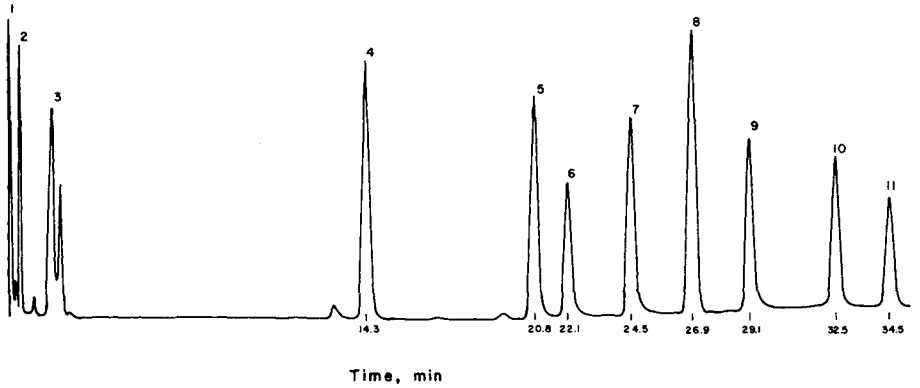


Fig. 1. Gas-chromatographic analysis of the TMS derivatives of a mixture of dicarboxylic acids, amino acids, and diamines (see text for peak assignments).

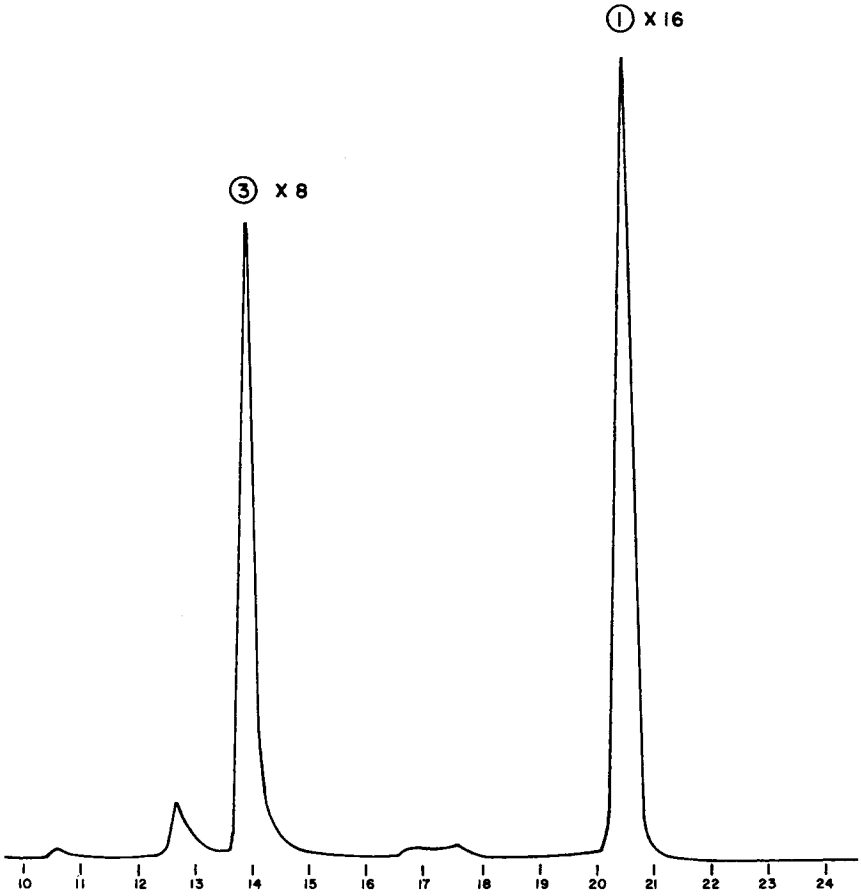
TABLE I
Calculated Compositions of Nylon 66 Based on GC Peak Areas and Possible Extent of Substitution in TMS Derivatives[a]

Number of TMS substituents on adipic acid	Mole percent of hexamethylenediamine based on number of TMS substituents indicated				
	0	1	2	3	4
0	63.8	52.2	44.1	38.2	33.6
1	72.5	61.9	54.1	48.0	43.1
2	77.8	68.4	61.0	55.1	50.2

[a] Peak areas for the TMS derivatives, x, were converted to calculated peak areas for each monomer, y, from their molecular weight ratios: $y = x(MW_y/MW_x)$.

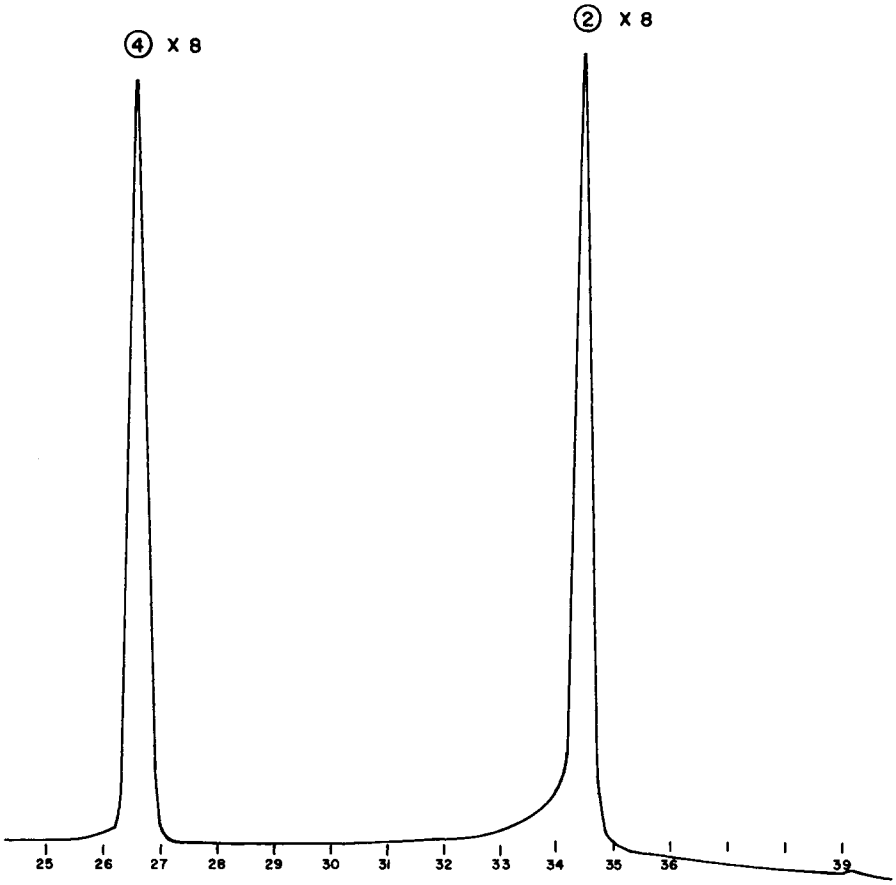
nation of derivatives which agrees with this expected composition, based on the observed peak area ratios, was that in which the diacid component was present in the effluent as the bis-TMS derivative and the diamine as the tetrakis-TMS derivative. By the same token, amino acid components in derivatized mixtures should be present as tris-TMS derivatives and will be assumed to be so in calculations based upon peak areas.

Figure 1 demonstrates the versatility of this approach in analyzing a mixture of nylon monomers. The chromatogram shown in this figure was obtained by the trimethylsilylation of a mixture of 5 mg of each of amino acids, diamines, and dicarboxylic acids, and the peaks represent either the reagents used for derivative formation or the derivatives of the following amines or acids: (1) acetonitrile, (2) triethylamine, (3) N,O-bis(trimethylsilyl)acetamide, (4) adipic acid, (5) 6-aminocaproic acid, (6) azelaic acid, (7) sebacic acid, (8) hexamethylenediamine, (9) dodecanedioic acid, (10) 11-aminoundecanoic acid, and (11) 12-aminolauric acid. It was observed, in this regard, that TMS derivative formation could be carried out more readily with the hydrochloride salt than with the amine itself.



(a)

Fig. 2. Gas-chromatographic analysis of terpolymer of nylon 6 (39%), nylon 12 (26%), and nylon 66 (35%).



(b)

Fig. 2. (*Continued from previous page.*)

This technique has been applied to a number of copolyamides by hydrolyzing the polymers, isolating the solid monomeric components (as described in the Experimental section), and converting these to their BSA derivatives as a mixture. The results for a typical analysis are shown in Figure 2 for a terpolymer of 6-aminocaproic acid (nylon 6 units), 12 aminolauric acid (nylon 12 units) and adipic acid–hexamethylenediamine (nylon 66 units). Quantitative analysis of the chromatograms of Figure 2 indicates that this sample is a terpolymer of 39% nylon 6, 26% nylon 12, and 35% nylon 66.

Composition–Retention Time Relationships

An interesting result of these analyses was the quantitative relationship between monomer composition and GC retention time. This relationship was found to be linear in a plot of retention time as a function of the number of carbon atoms in the monomer. Such plots are shown in Figure 3 for a series of ω-amino acid monomers and in Figure 4 for a series of aliphatic dicarboxylic acid monomers. Data for Figure 3 were obtained either by hydrolysis of the lactams to the amino acids for the 7-, 8-, and 10-carbon compounds, or by hydrolysis of the

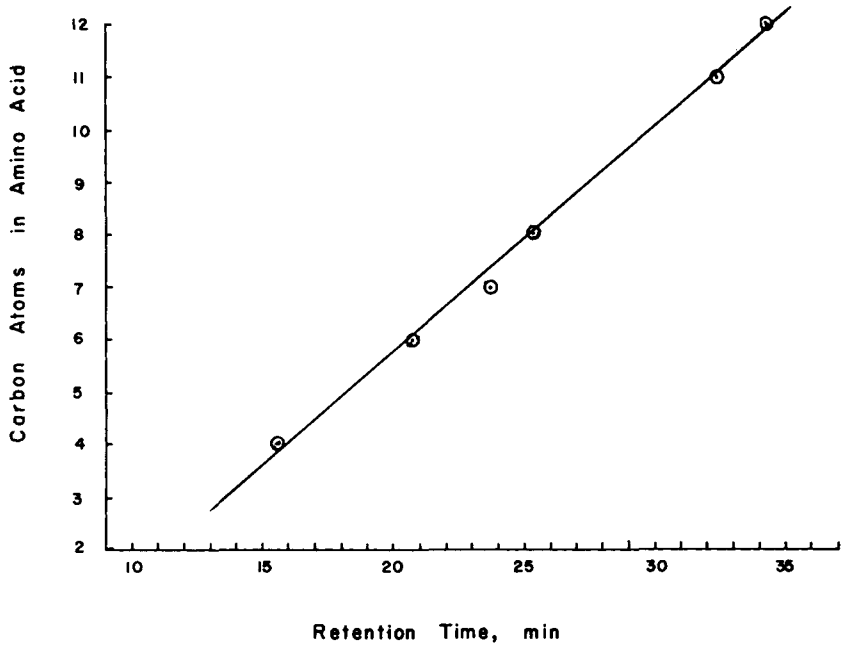


Fig. 3. Retention time as function of carbon atom content in the gas-chromatographic analysis of TMS derivatives of ω-amino acids.

polyamides for the 2-, 4-, 5-, 6-, 11-, and 12-carbon compounds. Neither the lactams nor the polyamides were available for the 3- and 9-carbon compounds.

Determination of Copolyester Compositions

The hydrolysis–gas-chromatographic analysis described above for polyamides was modified and extended to the analysis of copolyesters. The compositions of several copolymers of poly(ethylene terephthalate–*co*–succinate), P(ET/ES), were determined by this procedure and verified by NMR analysis. The results of these analyses are recorded in Table II.

Table II lists the weight percent terephthalate contents determined by GC analysis as compared to NMR analysis based on either the diacid units or the glycol units. The data show that all three values are in close agreement, and the experimental error for the GC analysis may be estimated to be within ±1.5% of the true value.

EXPERIMENTAL

Materials

Dimethyl Terephthalate (DMT). Practical-grade DMT obtained from Eastman Chemical Co. was purified by double recrystallization. Thus, 50 g DMT was dissolved with heating in 1000 ml absolute ethanol, filtered, heated to redissolve the DMT, and allowed to stand at room temperature for 24 hr. Crystals so obtained were collected by suction filtration and washed with two 100-ml

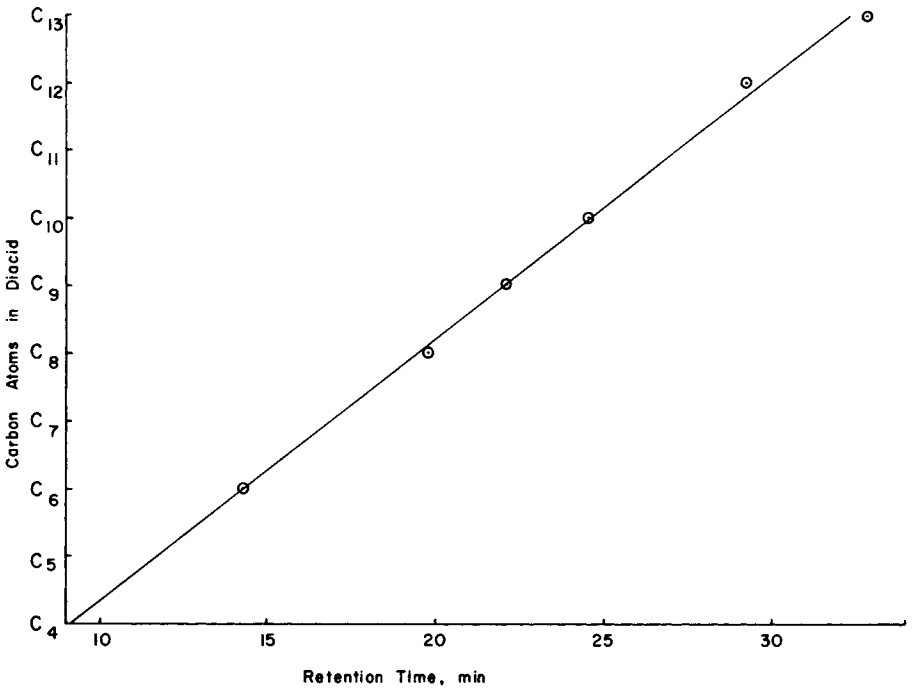


Fig. 4. Retention time as function of carbon atom content in the gas-chromatographic analysis of TMS derivatives of dicarboxylic acids.

TABLE II
Comparison of Analyses of Various Samples of Poly(ethylene Terephthalate–co–Succinate) by GC and NMR

Copolymer sample	wt. % T by GC[a]	wt. % T by NMR, acid residues[a]	wt. % T by NMR, glycol residues[a]
1	83.0	82.5	82.3
1A[b]	84.2	82.5	82.3
2	85.4	85.0	84.6
3	75.5	76.0	76.8
4	79.4	79.7	81.5
5	87.3	85.9	85.3
6	90.8	91.3	91.7

[a] T = Terephthalate units.
[b] Duplicate determination of copolymer 1.

portions of cold (0°C) ethanol. The DMT from the first recrystallization was subjected to a repetition of the above process, and the crystals were dried 18 hr at 40°C in a vacuum oven. Yield 38 g, mp 143°C.

Dimethyl Succinate (DMS). DMS obtained from Eastman Chemical Co. was mixed with 10 wt.% predried anhydrous magnesium sulfate and allowed to stand overnight. The mixture was transferred to a distillation flask, and the DMS was vacuum distilled. The fraction amounting to the middle 70% was collected at a constant boiling point of 37–38°C at 1 Torr.

N,O-Bis(trimethylsilyl)acetamide (BSA). BSA was obtained from Pierce

Chemical Co. in 1-ml ampoules. The ampoules were stored in the refrigerator, and any unused portion from an open ampoule was discarded.

Ethylene Glycol. Under a dry nitrogen atmosphere, 10 g freshly cut sodium was dissolved in 1 liter ethylene glycol; and after refluxing the mixture for 2 hr under nitrogen, it was cooled and vacuum distilled. The first 15% and last 25% were discarded. The boiling point of the middle fraction was 51°C at 0.8 Torr.

Trifluoroacetic Acid (TFA). For use as a reprecipitation solvent, TFA obtained from Aldrich Co. in 99.5% purity was used without additional purification. For the NMR measurements, to each 500-g bottle of 99.5% TFA was added 2% (w/v) hexamethyldisiloxane as a reference, and this mixture was used for obtaining all NMR spectra. Periodically, NMR spectra were obtained on this mixture to ensure against contamination.

Triethylamine. Triethylamine was purified by refluxing over barium oxide for 3 hr and distilled into a dry, sealed bottle; the boiling point was 88–89°C.

Acetonitrile. The acetonitrile used was the silination-grade solvent provided by Pierce Chemical Co. in a septum bottle.

Preparation of Copolyesters

Copolyesters were prepared by melt polycondensation to ensure a random distribution of monomer residues. All of the polymerization reactions were performed in the same manner, and only the preparation of the 74% terephthalate content sample of poly(ethylene terephthalate–*co*–succinate) will be detailed here as an example. Monomer ratios, reaction times, and temperature for the other copolymerization reactions are collected in Table III.

The polymerization reactor was a 100-ml, one-neck, round-bottom flask fitted with a nitrogen inlet, a sealed stirring adapter, condensor, and vacuum outlet. After charging 25 g DMT (0.129 mole), 8 g DMS (0.055 mole), 25.1 g ethylene glycol (0.368 mole), and 0.0050 g calcium acetate dihydrate to the flask, the system was purged with nitrogen for 15 min before being lowered into a constant-temperature bath maintained at 160°C. After 3 hr reaction time methanol evolution had ceased and the bath temperature was raised to 265°C over 45 min. Upon reaching this temperature 0.011 g antimony trioxide was added and vacuum was applied slowly over a period of 30 min, until a pressure of less than 0.1 Torr was reached. These conditions were maintained for 7 hr, and the flask was removed from the bath and allowed to cool under a nitrogen atmosphere. The polymerization catalyst was removed by dissolving the copolymer in trifluoroacetic acid and precipitating into a tenfold excess of methanol. The polymer was recovered by filtration, dried in a vacuum oven for 24 hr, ground in a Wiley mill to pass a 20-mesh sieve, and annealed for 5 hr over refluxing bis(methoxyethyl) ether (bp 162°C).

Analytical Procedures

Polyamide and Lactam Analyses. Samples of polyamides or lactams to be analyzed were ground into powders and hydrolyzed by refluxing in aqueous 6*N* hydrochloric acid for 8 hr. The resulting solution was evaporated to near dryness in a distillation apparatus being careful to vent the HCl fumes. Final drying

TABLE III
Reaction Conditions for P(ET/ES) Copolymerization Reactions

Polymer sample	Feed compositions, g (moles)			Reaction Conditions			
				First stage[a]		Second stage[b]	
	DMT	DMS	EG	hr	°C	hr	°C
1	13.3 (0.068)	2.5 (0.017)	12.0 (0.215)	3	160	5½	240
2	19.6 (0.100)	4.86 (0.033)	17.3 (0.279)	3	160	7½	260
3	19.6 (0.100)	4.23 (0.029)	16.9 (0.273)	4	160	10	250
4	25.0 (0.129)	8.0 (0.055)	25.1 (0.368)	3	160	7	265

[a] Catalyst: 0.16% calcium acetate dihydrate, based on total weight of esters.
[b] Catalyst: 0.03% antimony oxide based on total weight of esters.

was accomplished in a heated vacuum oven. The residue was washed with water and redried several times to ensure the removal of HCl. As a final drying step, where necessary, the residue was subject to distillation with methylene chloride to azeotropically remove any remaining water. A 20-mg sample of the solid hydrolyzate was mixed with 300 μl BSA, 60 μl triethylamine, and 300 μl acetonitrile in a conical vial equipped with a magnetic stirrer. The vial was purged with dry nitrogen, sealed with a septum, and heated to 90°C for 1–2 hr. After cooling, a 1-μl sample was injected into a Hewlett–Packard 5700A gas chromatograph under the following conditions: column, 10% SE-30, ⅛ in. × 6 ft; carrier gas, helium, 20 ml/min; injector, 250°C; detector, 250°C; oven, 120–300°C at 4°C/min. Quantitative determination of the components was made by measuring peak areas.

Polyester Analysis. The P(ET/ES) copolymers were ground to pass a 20-mesh sieve, and a 0.2-g sample was placed in a 25-ml Erylenmeyer flask and saponified at 85°C with 5 ml of 1*N* aqueous NaOH for 36 hr. One ml of the saponificate solution was transferred to a conical vial and slowly evaporated to dryness. After drying the sample was carefully neutralized with 3*N* HCl, taking care not to allow the exothermic acid–base reaction to cause the contents of the vial to boil over. Drying of the sample was accomplished in an air oven maintained at 40°C. If the oven temperature was above 40°C, succinic acid could codistill, and all samples dried above this temperature were very low in succinate

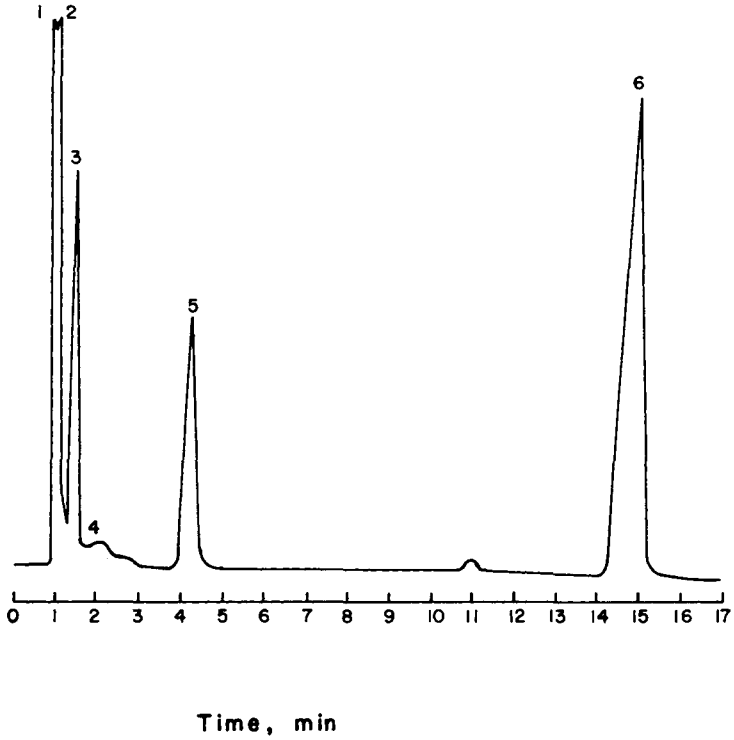


Fig. 5. Gas-chromatographic analysis of a copolyester of terephthalic acid and succinic acid with ethylene glycol; peak assignments of TMS derivatives or reactants and retention times in minutes: (1) acetonitrile, 0.9; (2) triethylamine, 1.0; (3) N,O-bis(trimethylsilyl)acetamide, 1.3; (4) ethylene glycol (TMS), 2.0; (5) succinic acid (TMS), 3.9; (6) terephthalic acid (TMS), 14.1.

content. When dry, the sample was washed with distilled water to remove residual HCl, redried, and finally azeotropically dried with methylene chloride. Final drying was accomplished over P_2O_5 for 12 hr in a vacuum oven. The reaction vials were sealed with rubber septa, and 60 μl triethylamine and 300 μl acetonitrile were injected. The contents were stirred for 20 min under a slow stream of predried nitrogen, and 400 μl BSA was added. The reaction was carried out for 10 hr at 65°C, after which the samples were chromatographed directly. A Varian Aerograph 1520 gas chromatograph with 5 ft × 1/8 in. columns of 10% SE-30 on Chromasorb W was employed for this analysis with the following operating conditions: injector, 250°C; detector, 250°C; column temperature program: 120°C for 3 min, 4°C/min for 3 min, 12°C/min for 3 min, hold isothermal until terephthalic acid peak elutes; carrier gas, helium at 25 ml/min; thermal conductivity detector.

The composition of the copolymers was determined by comparison to a calibration curve constructed by analyzing weighed mixtures of succinic and terephthalic acid by the above procedure. A typical chromatogram of the TMS derivatives is shown in Figure 5, in which the identity of the various peaks and their retention times are noted.

NMR Analysis. Samples of the P(ET/ES) copolymers were prepared by dissolving 0.1 g of the polymer in 1 ml trifluoroacetic acid with 2% hexamethyldisiloxane as internal standard. The spectra were recorded at 70°C using a Perkin–Elmer R-32 (90 MHz) NMR. The areas of the various resonance peaks were determined by integration for an average of five scans of the 100 Hz expanded-scale spectra.

The NMR spectrum of a P(ET/ES) copolymer consists of five sharp singlets as shown in Figure 6, one for each diacid unit and one for each of the three pos-

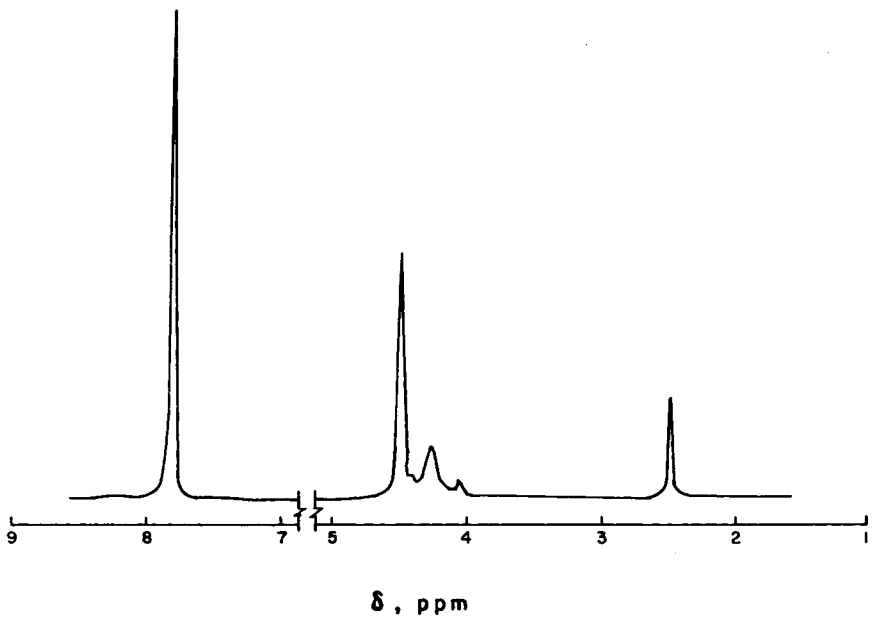


Fig. 6. NMR spectrum of poly(ethylene terephthalate–*co*—succinate); peak assignments: aromatic H, 7.78 ppm; glycol methylene H: T–G–T, 4.49 ppm; T–G–S, 4.29 ppm; S–G–S, 4.09 ppm; succinate methylene H, 2.46 ppm.

sible types of ethylene glycol dyads. The chemical shifts for these peaks are given in Figure 6. Because the terephthalate (T) and succinate (S) units each have four essentially equivalent protons, the composition of the copolymers could be calculated using eqs. (2):

$$\%T = A_T/(A_T + A_S) \qquad \text{or} \qquad \%S = A_S/(A_T + A_S) \tag{2}$$

where A_T is the area of the terephthalate unit peak and A_S is the area of the succinate unit peak. To verify the composition, eqs. (3) and (4) may also be used[5]:

$$\%T = TT + \tfrac{1}{2}(TS) \tag{3}$$

$$\%S = SS + \tfrac{1}{2}(TS) \tag{4}$$

where TT, SS, and TS are the mole fractions of glycol (G) methylene peaks in the T–G–T, S–G–S, and T–G–S dyads, respectively. The mole fractions were determined by dividing the individual intensities by the total intensity of all the glycol peaks combined.

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References

1. T. Okumoto, S. Tsuge, F. Yamamoto, and T. Takeuchi, *Macromolecules*, **7**, 376 (1974).
2. E. R. Blakley, *Anal. Biochem.*, **15**, 350 (1966); J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Am. Chem. Soc.*, **88**, 3390 (1966); J. P. Shyluk, C. G. Youngs, and O. L. Gamborg, *J. Chromatogr.*, **26**, 268 (1967).
3. C. W. Gehrke and K. Leimer, *J. Chromatogr.*, **57**, 219 (1971).
4. S. Mori, M. Furusawa, and T. Takeuchi, *Anal. Chem.*, **42**, 138,959 (1970).
5. R. Yamadera and M. Murano, *J. Polymer. Sci. A1*, **5**, 2259 (1967).

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