Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Degradable Polymers. IV. Degradation of Aliphatic Thermoplastic Block Copolyesters

Ann-Christine Albertsson[a]; Olle Ljungquist[a]
[a] Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden

To cite this Article Albertsson, Ann-Christine and Ljungquist, Olle(1988) 'Degradable Polymers. IV. Degradation of Aliphatic Thermoplastic Block Copolyesters', Journal of Macromolecular Science, Part A, 25: 4, 467 — 498
To link to this Article: DOI: 10.1080/00222338808053379
URL: http://dx.doi.org/10.1080/00222338808053379

J. MACROMOL. SCI.–CHEM., A25(4), pp. 467-498 (1988)

DEGRADABLE POLYMERS. IV. DEGRADATION OF ALIPHATIC THERMOPLASTIC BLOCK COPOLYESTERS

ANN-CHRISTINE ALBERTSSON and OLLE LJUNGQUIST

Department of Polymer Technology
The Royal Institute of Technology
S-100 44 Stockholm, Sweden

ABSTRACT

Three block copolymers of poly(ethylene succinate) and poly(tetramethylene glycol) with about 20, 54, and 59 mol% polyether have been prepared and subjected to hydrolytic degradation at 37°C. The sample containing 59 mol% showed drastic changes in the properties after 3 months of degradation, whereas the other samples exhibited only minor changes. The tensile strength was completely lost, the molecular weight had decreased to 7% of the original value, and the crystallinity (measured as heat of fusion) had more than doubled. IR and ^{1}H-NMR analyses showed that the rates of release of the different polymeric blocks varied throughout the period of hydrolytic degradation. Fibers of the block copolymer poly(ethylene succinate)/poly(tetramethylene glycol) with poly(tetramethylene glycol) fractions ranging from 20 to 50 mol% have been analyzed by ^{13}C NMR to determine the molecular weights of the PES blocks and by reflection IR, ESCA, and SEM to investigate the surface composition. The molecular weights of the polyester blocks were inversely proportional to the mol% of polyether, and the values were in agreement with theoretical calculated values. The surface concentration of the polyether was found to be higher than that in the bulk and also independent of the mol% polyether in the range of study. A degradation mechanism is proposed which involves a combined effect of surface erosion and hydrolytic attack on the ester linkages connecting the amorphous polyether and the crystalline polyester blocks.

INTRODUCTION

In modern surgery there is a great need for materials that are similar to human tissues with respect to tensile strength and elasticity and which are at the same time slowly absorbable [1]. Biodegradable devices are especially valuable since they eliminate the need for a second operation to remove them after their tasks are fulfilled.

The first commercially available degradable materials were stiff polyesters such as poly(glycolide) (PGA) [2] and [poly(glycolide/lactide) 90/10%] PGA/PLA [3]. Later, polyesters like poly(*p*-dioxanone) (PPD) [4] and most recently poly(glycolide)-*b*-poly(trimethylene carbonate) PGA/PTMC [5] have been found to be more useful because they show more flexibility. All of these materials but the first are copolymers: PPD is an alternating ester/ether copolymer of ethylene glycol and glycolic acid; PES/PTMC is a block copolymer of an aliphatic polyester and an aliphatic polycarbonate.

Present-day research seems to be striving toward degradable materials that are more elastic. The best way to increase elasticity seems to be to combine amorphous and crystalline blocks in the polymeric structure, i.e., to synthesize a block copolymer.

After the first tests with a degradable aliphatic homopolyester, poly(tetramethylene adipate) (PTMA) [6], the present series continued with a block copolymer poly(ethylene succinate)-*b*-poly(ethylene glycol) (PES/PEG) [7]. PES/PEG gave fibers that degrade too rapidly. Hydrolytic degradation, presumably in the amorphous parts, induced a rapid loss of tensile strength (to 7% of the original value in 10 d) although there was no significant weight loss. The hydrolysis seems to involve chain scission, as shown by GPC, and a "selective" degradation of the amorphous parts, as shown by DSC and ^{1}H NMR.

PES/PEG copolymers (and other aliphatic block copolyesters) have been made by Fradet and Maréchal [8], but only a low molecular weight polymer seems to have been obtained, and neither mechanical nor degradation data were reported.

It was the objective of this work to decrease the degradation rate of the copolymers, and the hydrophilic poly(ethylene glycol) groups were replaced by the more hydrophobic poly(tetramethylene glycol) segments. The synthesis of these block copolymers and their physical and chemical properties were described in the third paper in this series [9]. The copolymers were polymerized with six different polyether feeds, ranging from 21.1 up to 53.3 mol%. The resulting poly(ethylene succinate)-*b*-poly(tetramethylene glycol) (PES/PTMG) polymers were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), and tensile strength measurements. The molar compositions of the polymers were determined by NMR and IR and showed the predicted polymer composition. Fibers for tensile strength measurements were extruded, and samples for the dynamic mechanical thermal analyzer, DMTA, tests were compression molded. The crystallinity, the melting temperature, the fiber strength, and the elastic bending modulus were found to decrease with increasing polyether content, whereas the strain-to-break increased.

The present paper presents a study of hydrolytic degradation of the PES/PTMG copolymers. The changes in mechanical properties as a function of degradation time are discussed in relation to the changes in physical and chemical structure.

EXPERIMENTAL

A. Materials

Dimethyl succinate (synthesis grade), ethylene glycol (analysis grade), phenothiazine (synthesis grade), and tetraisopropyl orthotitanate (synthesis grade) were obtained from E. Merck (West Germany). Poly(tetramethylene glycol) (MW = 650) was obtained from Polyscience (U.S.A.). The glycols and the phenothiazine were used as received. The titanate and the succinate were purified by distillation, and the titanate was stored under nitrogen in sealed amber bottles.

B. Polymer Synthesis

The polymers were synthesized by polycondensation of dimethyl succinate (DMS), ethylene glycol (EG), and poly(tetramethylene glycol) (PTMG), as previously described [9]. The reagents (DMS (0.30 mol, 43.9 g), EG (0.39 mol, 24.0 g), PTMG, and the thermal stabilizer (phenothiazine, 0.001 mol, 0.2 g)) were added to a carefully dried 3-necked flask. Dry nitrogen was bubbled through the mixture for at least 15 min with rapid stirring, then tetraisopropyl titanate (0.5 mL) was added and the temperature raised to 150°C. When the condensation slowed (after approximately 6 h), the reaction flask was evacuated by replacing the combined distilling head and nitrogen inlet with a vacuum line. The pressure was slowly lowered to <50 Pa (0.5 mbar) and the temperature raised to 180°C. When the product was too viscous to stir (after approximately 12 h), the reaction was stopped by cooling the mixture to 110°C and raising the pressure to normal by introducing nitrogen. The resulting off-white viscous polyester was dissolved in dichloromethane, and the polymer was precipitated by dripping the solution into methanol.

Six block copolymers, A-F, were found to contain 20, 33, 34, 43, 54, and 59 mol% of PTMG, respectively, as determined by ^{1}H NMR (the accuracy was ±2 mol%). Three types of the block copolymer, A, E, and F, were used for the degradation studies. The results of the characterization of the original polymers are shown in the tables and figures at zero degradation time.

C. Polymer Degradation

Fibers of the block copolymer were extruded at 95°C in an extrusion device made in our workshop. The fibers were then drawn at room temperature, and the oriented products had diameters of 0.45 ± 0.05 mm. The fibers obtained were cut into 10 cm lengths. Three such pieces of each polymer were chosen at random and placed in each of a set of 25 mL Erlenmayer flasks containing 10.0 mL "pseudo extra-cellular fluid" (PSE) [10] (Table 1) thermally stabilized at 37°C in a shake incubator Type 3022 from GFC. The flasks were agitated at 90 rpm. One of the flasks containing each type of the polymers was opened after 3, 11, 19, 46, 87, and 172 days, the three fibers were withdrawn, carefully rinsed with distilled water, and characterized as described below.

This experimental design was chosen so that the PSE could be analyzed with respect to possible degradation products. In the discussion of the results, the longest degradation times are referred to as 12 and 25 weeks.

D. Polymer Characterization

The degraded fibers of the PES/PTMG block copolymers were subjected to tensile strength measurements while still wet. The pieces from this test were then dried, and DSC measurements were made on triplicate samples from each set of fibers. The remaining pieces were dissolved in chloroform and characterized by GPC, IR, and ^{1}H NMR. Triplicate samples were used for IR spectroscopy, tensile tests, and DSC analysis.

The tensile strength was measured on an Instron 1122 apparatus equipped with pneumatic grips (No. 2714-002).

For DSC analysis a Perkin-Elmer DSC-2 apparatus was used with a heating rate of 10°/min. The sample weight was approximately 5 mg.

A Waters 6000 A pump with two Shodex columns (GPC AC-80M/S) con-

TABLE 1. Composition of the Degradation Medium (PSE)[a]

Salt	Concentration, g/L
NaCl	5.55
KCl	0.37
$Ca(Ac)_2$	0.21
$MgSO_4 \cdot 7H_2O$	0.24
$Na_2HPO_4 \cdot 7H_2O$	0.36
Tris	3.63
NaN_3	0.20

[a] This solution was buffered at pH 7.3.

nected to a differential refractometer was used for GPC analysis with chloroform as the solvent. The flow rate was 1 mL/min. The analysis was carried out at 28°C with the solvent pressure at 4.6 MPa (650 psi). Polystyrene samples were used as calibration standards.

The Fourier transform IR (FTIR) spectrometer was a Perkin-Elmer 1710, with sample films deposited on NaCl windows.

For NMR analysis a Jeol JNM-PMX 60 SI spectrometer was used for ^1H NMR, and a Bruker WP-200 spectrometer for ^{13}C NMR. The fibers had been dissolved in deuterated chloroform.

To investigate the surface composition of the original fibers, a Spectratech multiple-internal-reflection (MIR) accessory was used for reflection IR spectroscopy with sample fibers on a KRS-5 crystal, and an ESCA spectrometer was used for the analysis of the outermost surface.

The ESCA equipment used was a Leybold Heraeus ESCA/Auger spectrometer LH 200. The polymer samples were dissolved in chloroform, and the solution was placed on palladium-sputtered aluminum plates. After the chloroform had evaporated, the plates were heated above the melting temperature of the polymers and then slowly cooled at room temperature, allowing the polymers to crystallize.

Scanning electron microscopic (SEM) studies were carried out using a Mini-SEM from International Scientific Instruments. The fibers were sputtered under the mildest conditions possible; the ionization voltage was 750 V, and the fibers were sputtered 10 times for 2 min, each sputtering followed by 2 min argon flushing.

RESULTS

Results of Mechanical Tests

The goal of this research has been to obtain an elastic, slowly degradable polymer. The PES/PTMG copolymers were synthesized to increase the degradation time and to retain the tensile strength for a longer time than had been observed with PES/PEG, which lost nearly all its tensile strength in less than 10 d. The results show that the PES/PTMG copolymers did indeed retain their strength for a longer period. Table 2 shows the tensile strength data for the three PES/PTMG. The tensile strength is plotted against degradation time in Fig. 1, and the strain-to-break is shown as a function of time in Fig. 2.

The data show clearly that the initial strength decreases, but that the initial strain-to-break increases, with increasing mol% PTMG. Sample E (54 mol% PTMG) appears to degrade less rapidly than Sample A (20 mol% PTMG) but Sample F (59 mol% PTMG) shows a drastic decrease between 12 and 25 weeks. During the first 12 weeks the strength of Sample A decreases from 140 to 119 MPa, of Sample E from 85 to 82 MPa, and of Sample F from 80 to 74 MPa, equivalent to 85, 96, and 89%, respectively, of the original value. When the tests were continued for 25 weeks, the tensile strength decreased to 84% for Sample A, and 73% for Sample E while Sample F lost its mechanical strength completely.

The strain-to-break also showed a variation in time dependence. For Sample A the strain-to-break decreased from 2.3 to 0.7 in 25 weeks. For Sample E, on the other hand, the change was not statistically significant. For Sample F the strain-to-break varied between 4.9 and 3.9 during the first 12 weeks but decreased to 0 after 25 weeks.

The greatest elongation is found in Sample F, the elongation increasing with the mole fraction of the polyether. Sample A shows a decrease in the first 2 weeks but a constant level thereafter. Sample E shows no statistically significant change, whereas the elongation of Sample F apparently decreases steadily and reaches 0 within 25 weeks. Since it was impossible to make triplicate tests at 19 and 46 days due to fiber slippage in the grips, the pattern of change within the first 12 weeks is not substantiated statistically.

Results of GPC

The change in molecular weight with increasing degradation time is shown in Table 3 and in Figs. 3A ($\bar{M}_n$) and 3B ($\bar{M}_w$).

TABLE 2. The Tensile Strength and Strain to Break of PES/PTMG Fibers Subjected to Hydrolytic Degradation in a Buffered Solution (pH 7.3) at 37°C[a]

Sample	Time, d	σ_b, MPa	ϵ_b, Δmm/mm$^{\circ}$
A-0	0	140 ± 10	2.3 ± 0.6
A-1	3	163 ± 10	3.5 ± 1.0
A-2	11	133 ± 20	1.3 ± 0.6
A-3	19	134 ± 9	0.8 ± 0.3
A-4	46	132 ± 6	1.2 ± 0.4
A-5	87	119 ± 9	0.9 ± 0.6
A-6	172	102 ± 10	0.7 ± 0.1
E-0	0	85 ± 4	2.9 ± 1.2
E-1	3	67 ± 7	3.2 ± 0.5
E-2	11	82 ± 1	4.2 ± 1.2
E-2	19	62 ± 1	2.7 ± 1.1
E-4	46	75 ± 11	2.8 ± 0.1
E-5	87	82 ± 9	3.7 ± 0.4
E-6	172	71 ± 6	3.8 ± 1.3
F-0	0	80 ± 6	4.9 ± 1.0
F-1	3	65 ± 4	7.1 ± 0.3
F-2	11	48 ± 6	5.4 ± 3.0
F-3	19	47	5.3
F-4	46	48	4.8
F-5	87	74 ± 10	3.4 ± 0.2
F-6	172	0	0

[a] Triplicate tests were made (where possible) and both mean and standard deviation values are given.

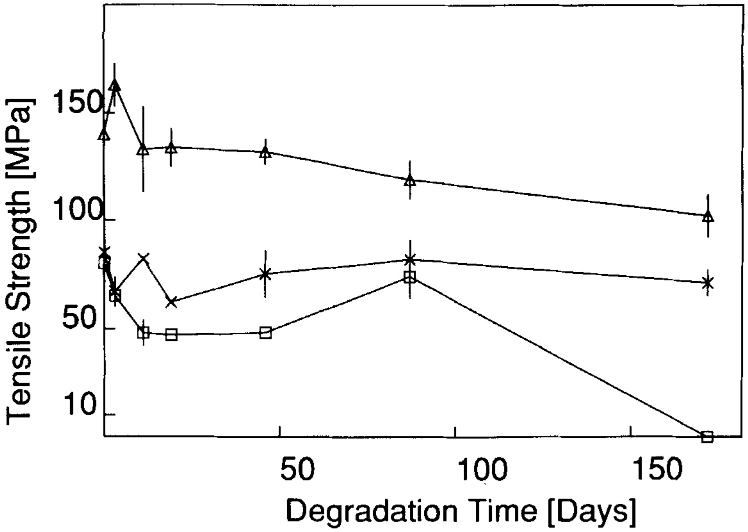


FIG. 1. The tensile strength of PES/PTMG fibers as a function of hydrolytic degradation time in a buffered solution (pH 7.3) at 37°C. Triplicate tests were made (where possible), and the vertical bars represent standard deviations. △ = A, X = E, and □ = F.

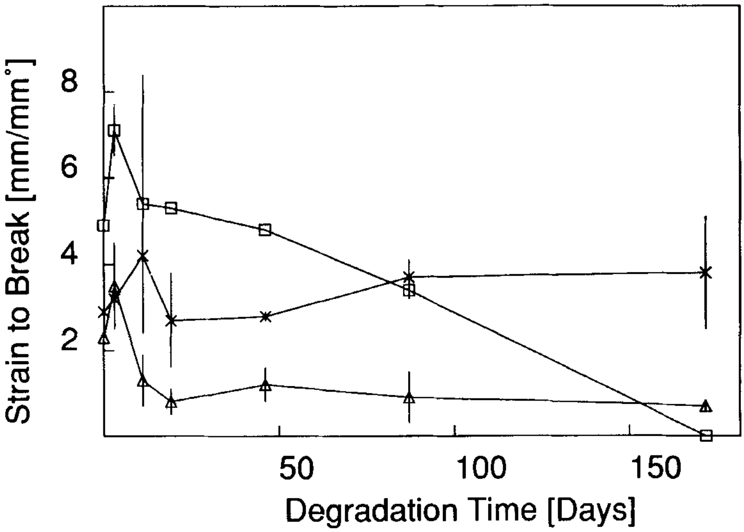


FIG. 2. The strain-to-break of PES/PTMG fibers as a function of hydrolytic degradation time in a buffered solution (pH 7.3) at 37°C. Triplicate tests were made (where possible), and the vertical bars represent standard deviations. △ = A, X = E, and □ = F.

TABLE 3. Number-Average and Weight-Average Molecular Weights Determined by GPC of PES/PTMG Fibers Subjected to Hydrolytic Degradation in a Buffered Solution (pH 7.3) at 37°C

Sample	Time, d	$\bar{M}_n$	$\bar{M}_w$
A-0	0	29 000	56 000
A-1	3	28 000	55 000
A-2	11	22 000	42 000
A-3	19	24 000	49 000
A-4	46	24 000	55 000
A-5	87	25 000	51 000
A-6	172	11 000	29 000
E-0	0	37 000	62 000
E-1	3	43 000	78 000
E-2	11	30 000	51 000
E-3	19	22 000	41 000
E-4	46	33 000	61 000
E-5	87	21 000	45 000
E-6	172	24 000	50 000
F-0	0	46 000	91 000
F-1	3	33 000	71 000
F-2	11	31 000	66 000
F-3	19	32 000	64 000
F-4	46	32 000	67 000
F-5	87	31 000	77 000
F-6	172	3 000	7 000

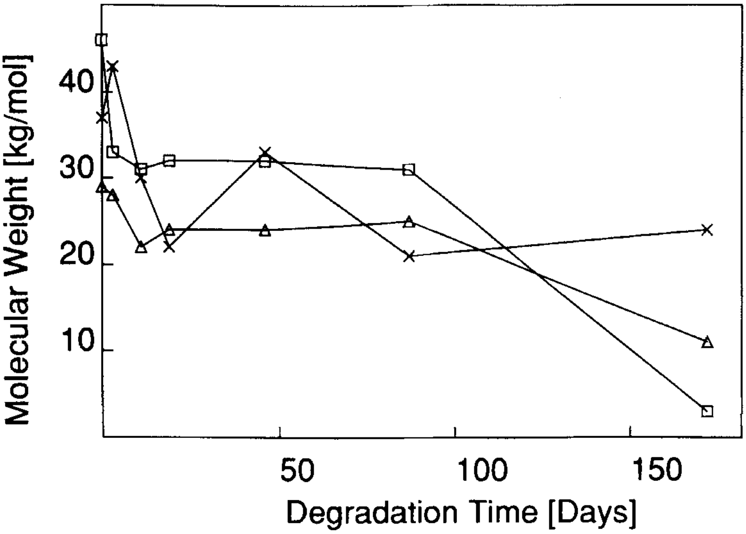


FIG. 3A. Number-average molecular weights of fibers of PES/PTMG block copolymers determined by GPC as a function of hydrolytic degradation time in a buffered solution (pH 7.3) at 37°C. △ = A, X = E, and □ = F.

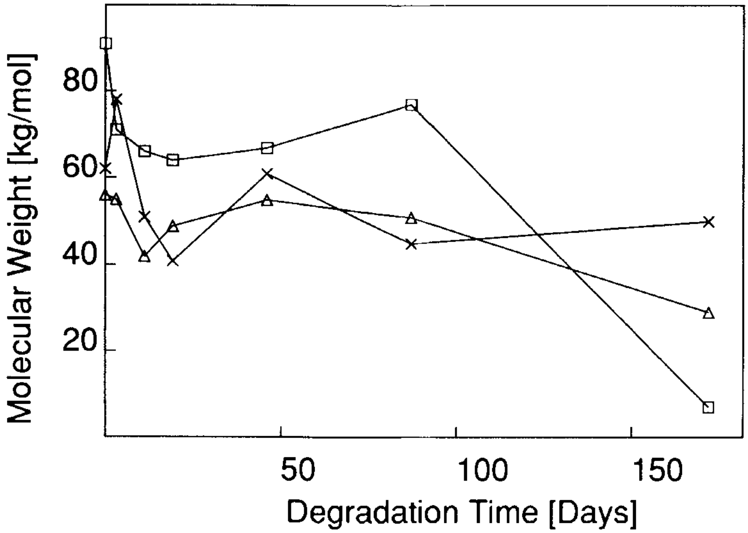


FIG. 3B. Weight-average molecular weights of fibers of PES/PTMG block copolymers determined by GPC as a function of hydrolytic degradation time in a buffered solution (pH 7.3) at 37°C. △ = A, X = E, and □ = F.

For Sample A, $\bar{M}_n$ decreases from 29 000 to 11 000 and $\bar{M}_w$ from 56 000 to 29 000 during 25 weeks. For Sample E, $\bar{M}_n$ decreases from 37 000 to 24 000 and $\bar{M}_n$ from 62 000 to 50 000 during the same period. Sample F, on the other hand, is extensively degraded with a decrease in $\bar{M}_n$ 46 000 to 3 000 and in $\bar{M}_w$ from 91 000 to 7 000.

The pattern of behavior is very similar for both $\bar{M}_n$ and $\bar{M}_w$. First there is a rapid change in molecular weight, followed by a second period of slower change, and finally a third stage of faster degradation. The curves thus exhibit the reported "S" shape, where the change in molecular weight is divided into three stages [11].

The first period covers the first 2 weeks after the fibers have been placed in the PSE degradation medium, and the second plateau stage lasts until the 87th day, the values in this phase being between 60 and 80% of the original values. The last samples were taken after 25 weeks of degradation, by which time the values had decreased drastically for Sample F to 7% of the original value. This decrease of molecular weight was also evident as a loss in tensile strength.

In the case of Sample F, Fig. 3B tends to a maximum at 12 weeks instead of a plateau level. This behavior has also been reported by Makino et al. [12], who subjected poly(*L*-lactide) microcapsules to hydrolytic degradation in various media and found a maximum in molecular weight after 75 d. In the present study it has not been possible to run multiple chromatograms, and this maximum may therefore lie within the limits of experimental error.

Results of DSC

The mechanical properties of a polymer are also very dependent on the crystallinity. In the present case, where the polymer is a block copolymer of an amorphous polyether and a crystalline polyester, the elastic properties depend heavily on the degree of crystallinity of the polyester.

DSC was used to investigate the crystallinity of the polymers by measuring the heat of fusion, ΔH_f, as the area of the peak corresponding to the melting of the polyester block. The data are presented in Table 4 and shown as a function of time in Fig. 4.

The crystallinity of Sample A was almost constant during the degradation period. The heat of fusion values varied between 49.9 and 51.7 J/g during 12 weeks and had increased to 60.2 J/g at 25 weeks. Sample E showed an increase from 34.3 to 39.9 J/g during the first 11 d, but the values then remained almost unchanged. Sample F showed a slow increase in the first 11 d, from 24.3 to 31.3 J/g, and then an even slower increase during the following

TABLE 4. Heat of Fusion (measured by DSC) of the Polyester Block in PES/PTMG Fibers Subjected to Hydrolytic Degradation in a Buffered Solution (pH 7.3) at 37°C[a]

Sample	Time, d	ΔH_f, J/g
A-0	0	51.6 ± 2.5
A-1	3	49.9 ± 1.8
A-2	11	51.1 ± 1.8
A-3	19	50.5 ± 0.8
A-4	46	51.7 ± 0.8
A-5	87	(35.0)
A-6	172	60.2 ± 1.1
E-0	0	34.3 ± 0.5
E-1	3	36.1 ± 1.5
E-2	11	39.9 ± 1.8
E-3	19	39.2 ± 0.3
E-4	46	39.2 ± 0.3
E-5	87	40.7 ± 2.0
E-6	172	39.7 ± 0.4
F-0	0	24.3 ± 0.5
F-1	3	29.3 ± 1.5
F-2	11	31.1 ± 1.9
F-3	19	32.7 ± 1.4
F-4	46	35.3 ± 2.2
F-5	87	34.5 ± 2.3
F-6	172	54.3 ± 3.5

[a] Triplicate tests were made, and means and standard deviations are given.

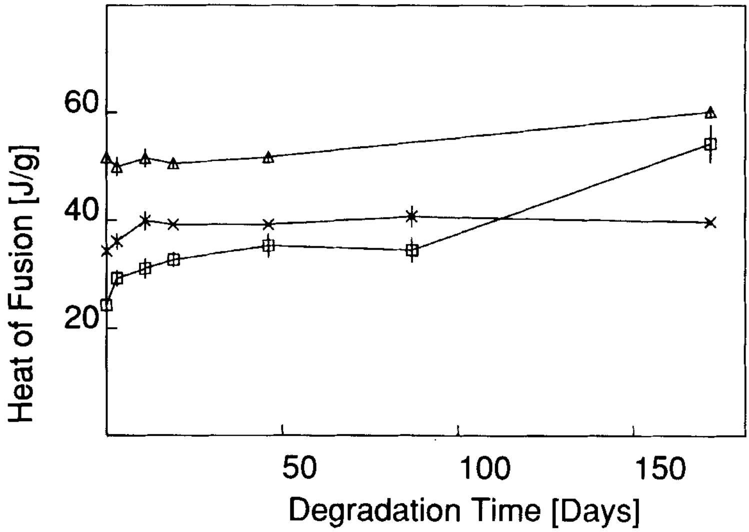


FIG. 4. The heat of fusion of the polyester block in PES/PTMG fibers determined by DSC as a function of hydrolytic degradation time in a buffered solution (pH 7.3) at 37°C. Triplicate tests were made, and the vertical bars represent standard deviations. △ = A, X = E, and □ = F.

11 weeks, but at 25 weeks ΔH_f had increased to 54.3 J/g, which was more than double the original value.

Sample A(20 mol% PTMG) has the highest value at the beginning of the degradation period followed by Sample E (54 mol% PTMG), while Sample F (59 mol% PTMG) has the lowest crystallinity; the higher the fraction of polyether, the lower the crystallinity. The curves maintain their relative positions throughout the degradation period, except for that of Sample F which at 25 weeks rises to the same level as that for Sample A. Samples E and F show a small increase at the beginning, whereas Sample A exhibits a very slow increase throughout the whole degradation period.

Results of IR and ^{1}H-NMR Spectroscopy

The mechanical properties are a function of the chemical composition. Two spectrographic methods, IR and ^{1}H NMR, were used to monitor the change in chemical composition of the blocks during the hydrolytic degradation. The chemical group of interest for IR is CH_2, which is present in both the polyether and the polyester. The spectra were normalized using the IR absorption

TABLE 5. Changes in the Chemical Composition of the Bulk of PES/PTMG Fibers Subjected to Hydrolytic Degradation in a Buffered Solution (pH 7.3) at 37°C

Sample	Time, d	IR,[a] $A(2970)/A(1735)$	NMR,[b] $I(1.7, 3.5\ \text{ppm})/I(\text{tot})$
A-0	0	0.09 ± 0.01	0.270
A-1	3	0.10 ± 0.01	0.254
A-2	11	0.10 ± 0.01	0.243
A-3	19	0.10 ± 0.02	0.195
A-4	46	0.06 ± 0.01	0.131
A-5	87	0.10 ± 0.02	0.193
A-6	172	0.08 ± 0.01	0.226
E-0	0	0.28 ± 0.01	0.545
E-1	3	0.29 ± 0.01	0.497
E-2	11	0.33 ± 0.02	0.498
E-3	19	0.29 ± 0.02	0.522
E-4	46	0.22 ± 0.01	0.450
E-5	87	0.28 ± 0.01	0.498
E-6	172	0.30 ± 0.01	0.522
F-0	0	0.33 ± 0.01	0.575
F-1	3	0.31 ± 0.01	0.560
F-2	11	0.29 ± 0.01	0.563
F-3	19	0.25 ± 0.01	0.531
F-4	46	0.23 ± 0.01	0.513
F-5	87	0.25 ± 0.01	0.553
F-6	172	0.18 ± 0.01	0.431

[a] Ratio of IR absorption of methylene groups at 2970 cm^{-1} relative to the absorption of carbonyl groups at 1735 cm^{-1}. At least five IR spectra of 50 scans each were recorded, and the means and standard deviation values are given.

[b] Ratio of NMR intensities of the polyether methylenes at 1.7 and 3.5 ppm to the total methylene integral.

of the ester carbonyls at 1735 cm^{-1} as internal standard, and the absorption of the methylene groups at 2850 cm^{-1} were followed so that the polyether fraction and its changes could be seen. Table 5 gives the mean values and the standard deviation of at least five independent spectra, each scanned 50 times, as the ratio of the methylene to the carbonyl absorption. This ratio for Sample A (0.09) can be regarded as constant up to 7 weeks, where there is a significant minimum (0.06). Samples E and F also exhibit minima at 7 weeks, the ratio for Sample E being 79% and for Sample F 68% of the original value.

NMR was used to follow the change in the integrals of the polyether methylenes at 1.7 and 3.5 ppm in relation to the total methylene integral since NMR can differentiate between polyether and polyester methylenes, whereas IR cannot. The ratio of the integral corresponding to the polyether to that of the total methylene is also given in Table 5. For Sample A the starting value is 0.27, and it decreases during the degradation period until 7 weeks, where it reaches a minimum at 0.13, which is 49% of the original. The value then increases and reaches 0.23 after 25 weeks. Sample E also shows a minimum at 7 weeks at 83% of the original. Sample F shows a smaller change to 89% of the original at 7 weeks, but at 25 weeks the value has decreased to 75%.

These data are plotted as the IR methylene/carbonyl ratio in Fig. 5 and as the NMR ether methylene/total methylene ratio in Fig. 6. The apparent minimum in the relative amount of the ether methylenes on the 46th day of degradation means that those results show a pattern different from that in any of the previous figures. It is important that, after 25 weeks, the value for Sample F decreases instead of increasing, as is the case for Samples A and E.

Surface IR Spectroscopy of Undegraded Fibers

The changes in properties resulting from the degradation indicated that it was important to characterize the surfaces and to see to what extent the original surfaces differed from the bulk material. To investigate the initial composition of the fiber surface, pieces of undegraded fiber were gently pressed against a KRS-5 crystal in a MIR accessory and 50 scans were recorded.

Comparison of these MIR-FTIR results with transmission IR-absorption data (Table 6 and Fig. 7) shows that the methylene fraction was much higher in the surface than in the bulk for Samples A-D. Sample E had a somewhat lower $A(2850)/A(1735)$ ratio in the surface than in the bulk, and Sample F had a much lower ratio in the surface. The low value for the reflection ratio in the case of Sample F may possibly be explained by the different IR spectra exhibited by this sample.

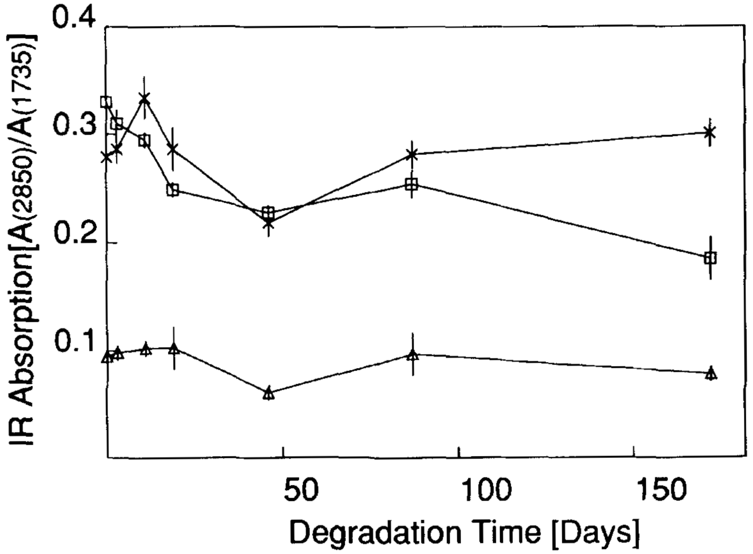


FIG. 5. The chemical composition of the bulk of PES/PTMG fibers, as determined by the ratio of IR absorption of methylene groups at 2850 cm^{-1} to the absorption of carbonyl groups at 1735 cm^{-1} as a function of hydrolytic degradation time in a buffered solution (pH 7.3) at 37°C. At least five spectra of 50 scans each were recorded, and the vertical bars represent standard deviations. △ = A, X = E, and □ = F.

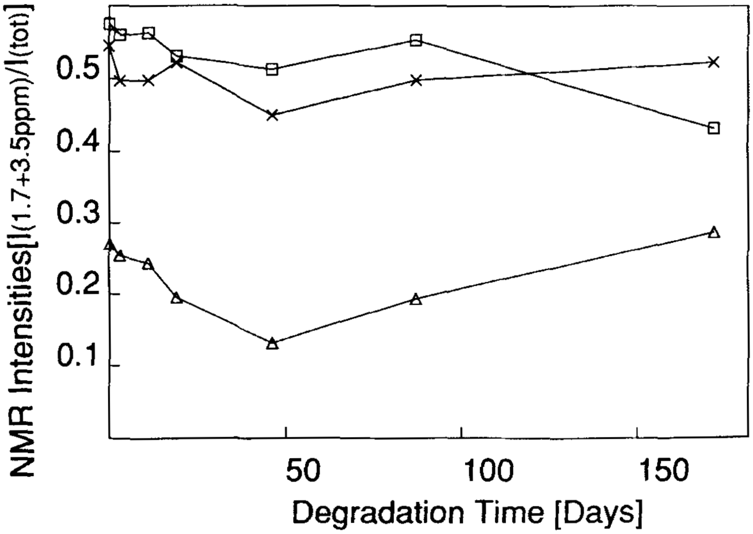


FIG. 6. The chemical composition of the bulk of PES/PTMG fibers as determined by the ratio of NMR intensities of the polyether methylenes at 1.7 and 3.5 ppm to the total methylene integral as a function of hydrolytic degradation time in buffered solution (pH 7.3) at 37°C. △ = A, X = E, and □ = F.

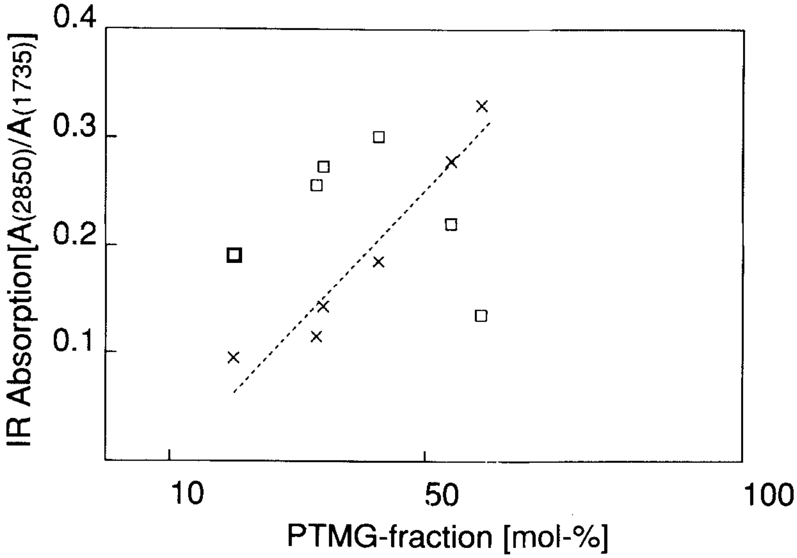


FIG. 7. The IR absorption of the methylene groups at 2850 cm^{-1} normalized with respect to the carbonyl group absorption at 1735 cm^{-1} plotted against the mol% PTMG of the bulk of the PES/PTMG fibers. X = transmission, □ = reflection IR.

TABLE 6. IR Absorption of the Methylene Groups at 2850 cm^{-1} Normalized with Respect to the Carbonyl Group Absorption at 1735 cm^{-1} Measured by Transmission and Reflection Spectroscopy

Sample	Mol%	Transmission	Reflection
A	19.9	0.095	0.191
B	32.9	0.115	0.256
C	34.0	0.142	0.274
D	42.6	0.185	0.301
E	54.0	0.279	0.221
F	58.7	0.330	0.135

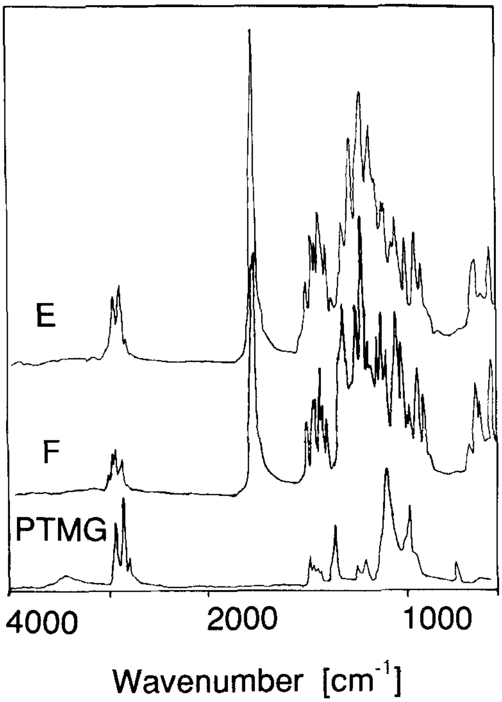


FIG. 8. Reflection IR spectrs of PES/PTMG fibers and the homopolymer spectra of PTMG. Samples E and F contain 54 and 59 mol%, respectively, of PTMG in the bulk.

Samples A-E had similar spectra, but the spectrum from Sample F differed, especially in the 2850 cm^{-1} region, and the absorbance ratio $A(2850)/A(1735)$ is therefore no longer an adequate indicator of the ether fraction. The spectrum of Sample F resembled instead the spectrum of the homopolymer of PTMG. Figure 8 shows the spectra of Sample E, Sample F, and PTMG homopolymer.

SEM Studies of Undegraded Fibers

This difference in surface structure was also seen by SEM. The micrographs in Fig. 9 show Samples E and F at two magnifications. It is evident that Sample E had a smooth surface, whereas the surface of Sample F was rugged or "flaked." This ruggedness may possibly be due to a fraction of the PTMG that is not fully incorporated in the system but, instead, acts as free homopolyether on the surface of the Sample F fibers.

ESCA of Undegraded Fibers

The penetration depth of the IR beam is dependent on the energy, and the apparent absorption at higher wavenumbers is, therefore, less than the true absorption [13]. The ratio $A(2850)/A(1735)$ is, therefore, too low, and the surface composition must be checked with an analysis method that does not have this drawback, such as ESCA.

ESCA provides an analysis of the outermost atomic layers, and absorption due to carbon and oxygen atoms is detected. The carbon/oxygen ratio may be determined by integrating the absorption peaks corresponding to the different atoms, the oxygen area being divided by ita appropriate sensitivity factor.

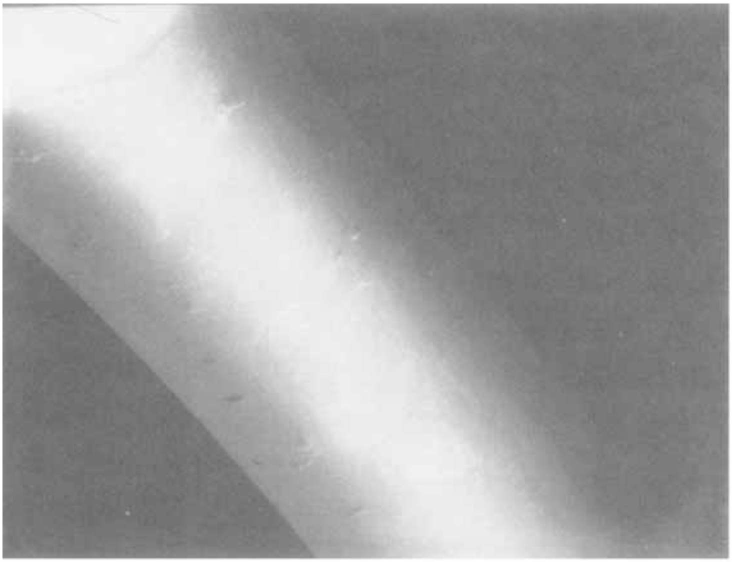
Since PES contains four oxygens and six carbons in the unit, and PTMG contains one oxygen and four carbons in its unit, a theoretical C/O value, $(C/O)_t$, can be calculated by

$$(C/O)_t = \frac{4y + 6(1-y)}{1y + 4(1-y)}, \tag{1}$$

where y is the mole fraction of polyether.

Table 7 presents the theoretical values and the values determined by ESCA. Clearly, the experimental C/O ratio is almost constant for the different samples and independent of the mol% PTMG in the bulk. The values are plotted against the bulk composition in Fig. 10. For all the samples analyzed, the experimental C/O values are higher than the broken line which represents the theoretical curve if the surface concentration were the same as that in the bulk of the material. This suggests that the surface polyether concentration is, in fact, higher than that of the bulk in all cases.

The ESCA spectra did, however, unexpectedly exhibit small silicon peaks, which may be due to the silicone grease used as sealant of the glass joints of the reaction flask. If so, the silicon is arising from dimethylsiloxane which contains one oxygen atom and two carbon atoms per silicon atom, and the experimental C/O values are corrected assuming this is the case.



a. — = 100μm

b. — = 2μm

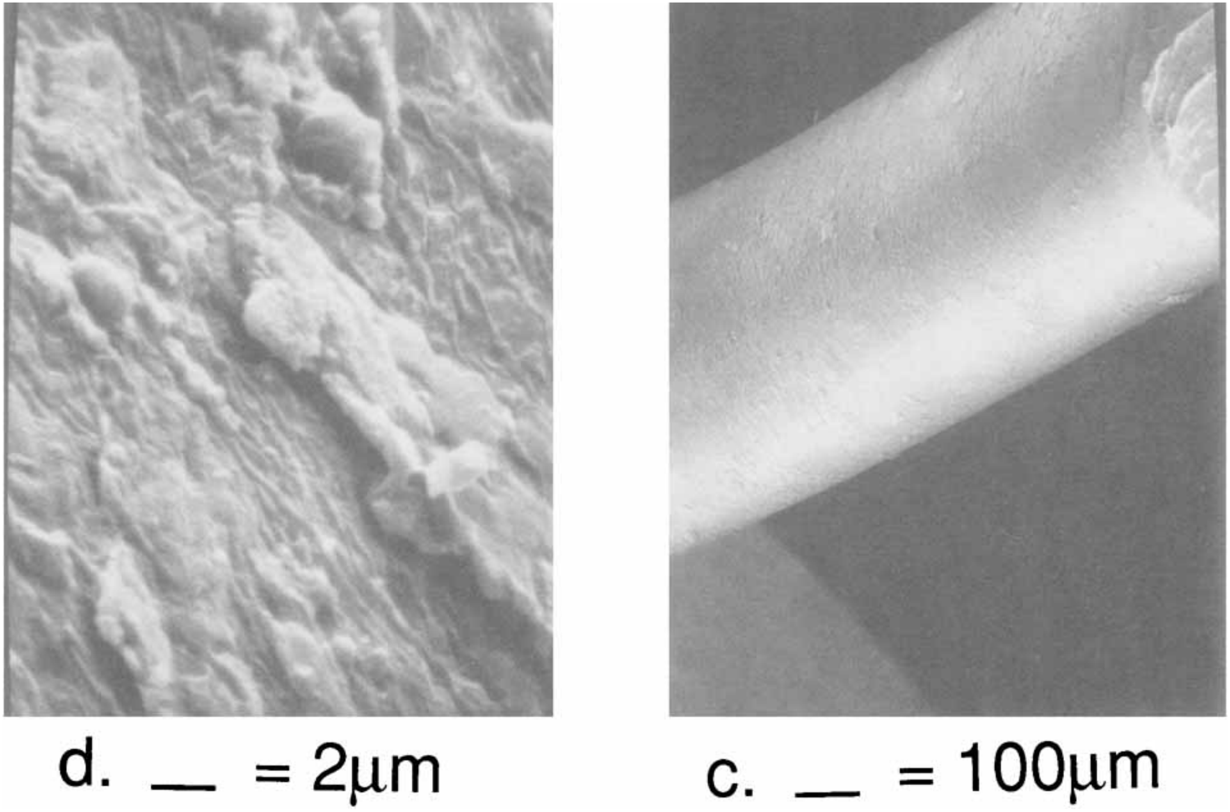


FIG. 9. SEM micrographs of PES/PTMG fibers. Samples E and F contain 54 and 59 mol%, respectively, of PTMG in the bulk. The *a* and *b* micrographs show Sample E at two magnifications, and the *c* and *d* micrographs show Sample F at two magnifications, indicated by the size bars.

TABLE 7. The Theoretical Carbon/Oxygen Ratio, $(C/O)_t$, and the Value Determined by ESCA, $(C/O)_{ESCA}$[a]

Sample	Mol%	$(C/O)_t$	$(C/O)_{ESCA}$
A	19.9	1.65	2.18, 2.25, 2.34
B	32.9	1.77	2.22, 2.25
C	34.0	1.79	–
D	42.6	1.89	–
E	54.0	2.07	2.23, 2.23, 2.42
F	58.7	2.16	2.24, 2.38

[a] The values are corrected with the sensitivity factors and the silicon peak due to the silicone grease used.

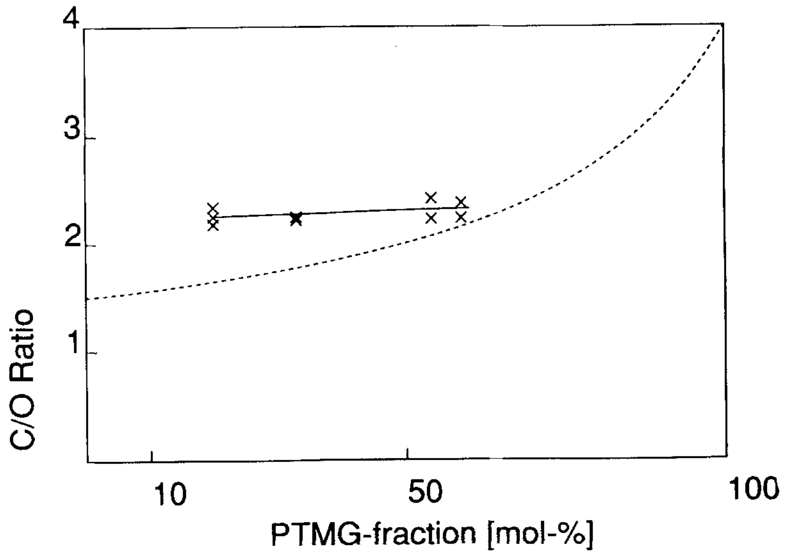


FIG. 10. The carbon/oxygen ratio for PES/PTMG copolymers melted onto aluminum plates as determined by ESCA, plotted against the mol% PTMG of the PES/PTMG bulk. The dotted line represents the theoretical curve for the C/O ratio in the bulk.

^{13}C-NMR Spectroscopy of Undegraded Material

Another property that might have affected the degradation rate was the molecular weight of the crystalline polyester block, and this property was investigated by ^{13}C-NMR spectroscopy of solutions of the original undegraded fibers.

The integrals of the NMR absorption peaks were used to calculate the molar composition of the block copolymers. The assignments of the peaks are given in Fig. 11 together with the structural formula. This structural formula of the block copolymer gives the following equations:

Number of ester units: $n = f\,(\mathrm{IC}/2)$, (2)

Number of ether units: $m = f\,(\mathrm{ID}/2 + \mathrm{IE}/2)/2$, (3)

Number of link groups: $L = f\,(\mathrm{ID}' + \mathrm{ID}'' + \mathrm{IE}' + \mathrm{IE}'')/4$, (4)

Number of blocks: $L/2$, (5)

Mole fraction of polyether: $y = (m + 2)/(m + 2 + n + (84/144))$, (6)

where f is the sensitivity factor of the equipment used, and IC, ID, . . . are the integrals of the C, D, . . . peaks. Table 8 shows the good agreement between the molar composition determined by ^{13}C NMR and that determined by ^{1}H NMR.

If the values of n and m are divided by $L/2$, the degrees of polymerization, *DP*, of the polymer blocks, *DP*(PES) and *DP*(PTMG), respectively, are obtained.

The number-average molecular weight of the polyether is

$$\bar{M}_n(\mathrm{PTMG}) = 72\,(DP(\mathrm{PTMG}) + 2), \tag{7}$$

and that of the polyester is

$$\bar{M}_n(\mathrm{PES}) = (DP(\mathrm{PES})144 + 84), \tag{8}$$

where 72 and 144 are the molecular weights of the polyether and the polyester units, respectively, 84 is that of the single ester unit, and the digit 2 accounts for the link groups.

Equation (9) gives the theoretical number-average molecular weight of the polyester, $(\bar{M}_n)_t$(PES), as a function of the mole fraction PTMG if m is constant. Assuming a value of 650 for $\bar{M}_n$ (PTMG) given by the manufacturer, the following expression is obtained:

$$(\bar{M}_n)_t(\mathrm{PES}) = (650)(144/72)((1/y) - 1) \tag{9}$$

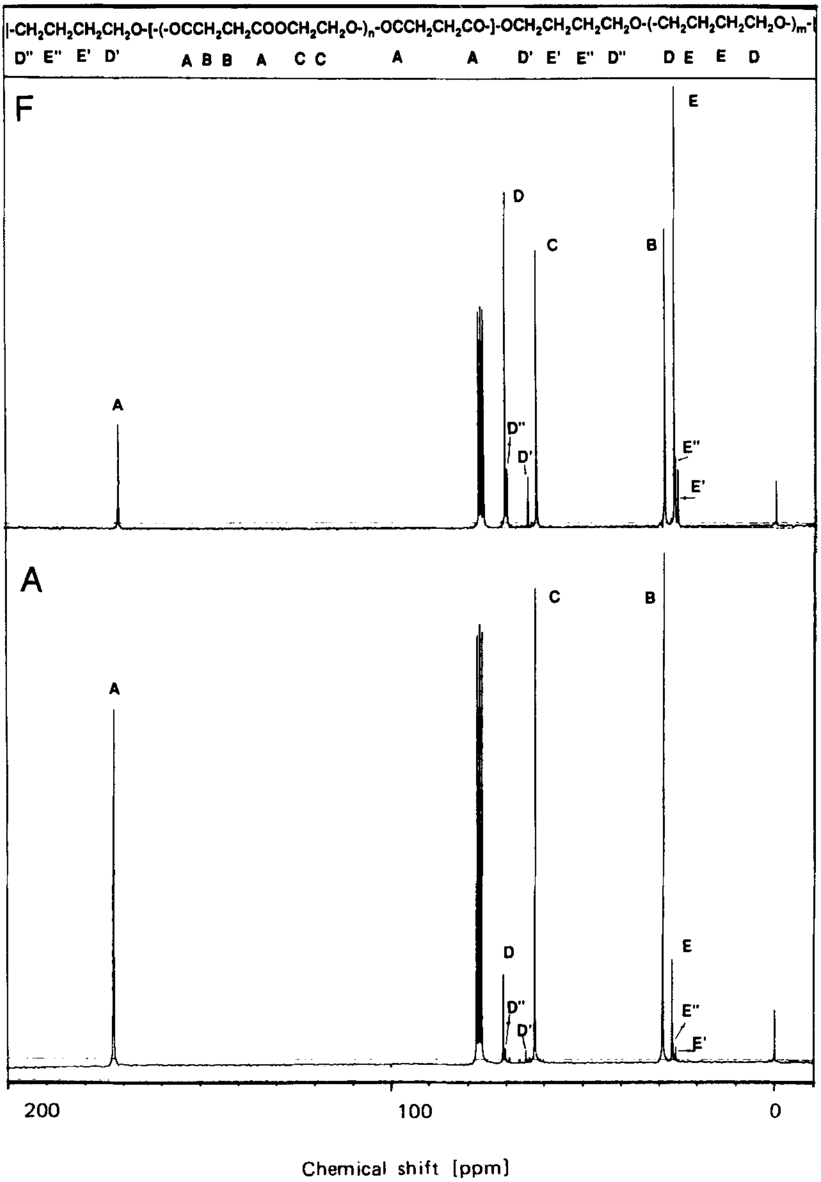


FIG. 11. ^{13}C-NMR spectra of PES/PTMG block copolymers and the assignments of the peaks. Samples A and F contain 20 and 59 mol% PTMG, respectively.

TABLE 8. Mol% PTMG Determined by ^{13}C-NMR Spectroscopy and the Calculated Molecular Weight of the Polyether and Polyester Blocks in PES/PTMG Fibers

Sample	PTMG, mol% ^{1}H NMR	PTMG, mol% ^{13}C NMR	m[a]	n[a]	$\bar{M}_n$ (PTMG)	$\bar{M}_n$ (PES)	$(\bar{M}_n)_t$
A	19.9	19.0	7.334	39.283	672	5741	5233
B	32.9	31.6	6.471	17.725	610	2636	2651
C	34.0	37.1	6.316	13.490	599	2027	2524
D	42.6	44.6	6.168	9.580	588	1464	1752
E	54.0	52.9	5.551	6.153	544	970	1107
F	58.7	58.8	6.769	5.565	631	885	915

[a] m is the mean number of mers in the polyether, n is the mean number of mers in the polyester.

The decrease in $\bar{M}_n$(PES) from 5700 to 890 with increasing mol% PTMG is shown also in Fig. 12. The experimental values agree reasonably well with the theoretical values although they are generally somewhat lower, mainly because the experimental $\bar{M}_n$(PTMG) figures are lower than the value of 650 given by the manufacturer. This may to some extent be due to the fact that the model structural formula does not take into account the effect of end groups, but this endgroup effect is nevertheless small since the polymers have relatively high molecular weights. Three small peaks in the NMR spectrum of Sample A (Fig. 11) are detected at 60-70 ppm, and they may be due to end groups. These peaks could, however, not be assigned.

^{13}C-NMR Spectroscopy of a Degraded Material

One of the materials, Sample F, has also been analyzed by ^{13}C-NMR spectroscopy to further investigate the change in the mol% polyether as a function of degradation time (Table 9). IR and ^{1}H-NMR spectroscopy indicated a minimum at 46 d of degradation, but in the ^{13}C-NMR analysis this minimum appears at 19 d, as shown in Fig. 13. This may indicate that the true minimum occurs somewhere between 19 and 46 d of degradation. However, the important fact is that this minimum is also seen by this spectrographical method.

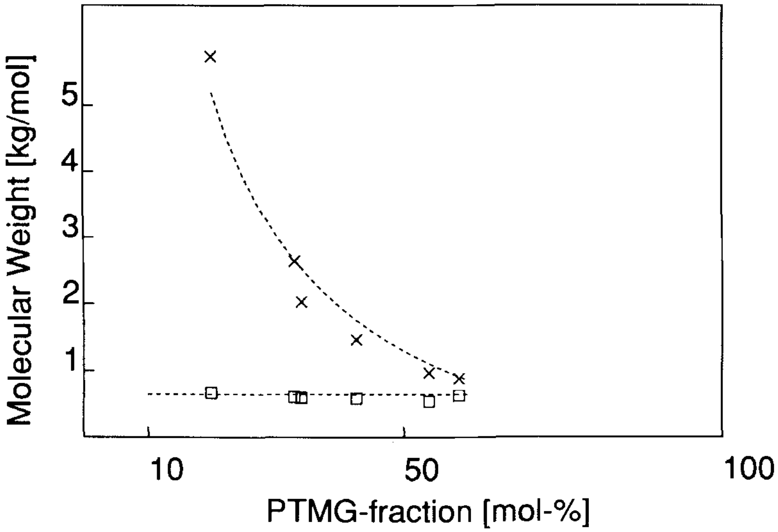


FIG. 12. Number-average molecular weights of the PES and the PTMG blocks in fibers of PES/PTMG block copolymers calculated from ^{13}C-NMR spectra, plotted against the mol% PTMG of the fibers. The dotted lines represent the theoretical values. X = PES and □ = PTMG.

TABLE 9. Mol% PTMG of Sample F at Increasing Degradation Time Determined by ^{13}C-NMR Spectroscopy

Sample	Time, d	PTMG, mol%
F-0	0	58.8
F-1	3	55.5
F-2	11	59.2
F-3	19	45.1
F-4	46	52.1
F-5	87	47.1
F-6	172	40.1

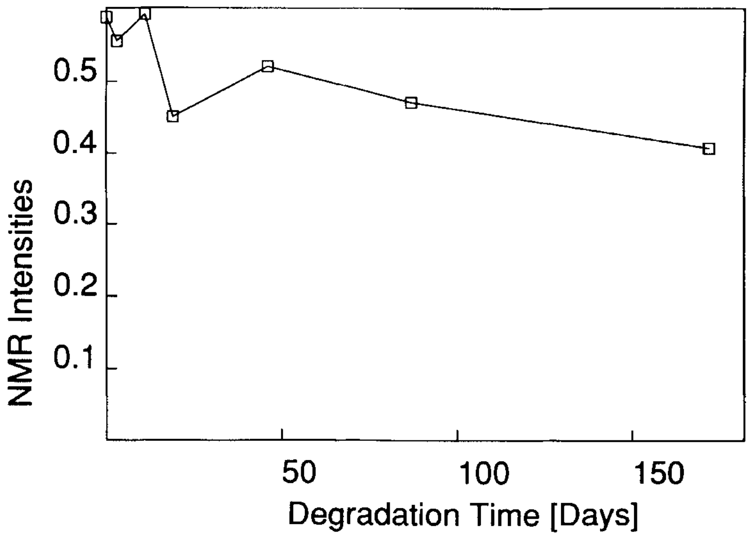


FIG. 13. The chemical composition of the bulk of the PES/PTMG fiber F as determined by the ^{13}C-NMR intensities of the C, D, and E peaks as described in Eq. (6) as a function of hydrolytic degradation time in buffered solution (pH 7.3) at 37°C.

DISCUSSION

The decrease in tensile strength is slower than that observed in the previous degradation study with the PES/PEG block copolymer [6], where the tensile strength decreased to less than 10% of the original values in only 10 d. The present work shows that the rate of degradation can be reduced by replacing the hydrophilic polyether with the hydrophobic poly(tetramethylene glycol).

The tensile strength (Fig. 1) slowly decreased during the degradation. No great changes in strength were observed for Samples A (20 mol% PTMG) and E (54 mol% PTMG), but Sample F (59 mol% PTMG) lost its tensile strength completely after 25 weeks.

The strain-to-break (Fig. 2) changed only slowly, and only Sample F failed due to degradation. Samples A and E had almost the same strain-to-break at the start, but Sample F had a strain value twice that of Sample E in spite of the fact that the chemical compositions differ by only 5 mol% PTMG.

All the block copolymers had a high molecular weight initially, and the differences were relatively small. The only sample which showed a loss in mechanical properties was Sample F, which had the highest initial molecular weight. The initial molecular weight is thus not sufficient to explain the degradation mechanism.

Another property which greatly affects the mechanical behavior of block copolymers is, of course, the crystallinity, here measured as the heat of fusion of the polyester blocks. The initial strain-to-break increases with increasing polyether fraction as the crystallinity decreases. When the crystallinity increases due to degradation, the strain decreases drastically. Sample F (59 mol% PTMG) suffers both a decrease in molecular weight and an increase in crystallinity after 25 weeks of hydrolytic degradation.

This behavior is quite similar to that of the polymer studied previously containing the same crystalline block, poly(ethylene succinate) (PES) but a different amorphous block, poly(ethylene glycol) (PEG). There is, however, a more pronounced change in the degradation rate than can be explained by the increase in hydrophobicity (PEG is water soluble whereas PTMG is not). The hydrolytic scission takes place in the amorphous part of the polyester, and this is still the same. The presence of water-insoluble PTMG appears, therefore, to protect the polyester from hydrolytic attack.

This idea is supported by the reflection IR and ESCA data which suggest that the surface of the PES/PTMG fibers has been enriched in the polyether. If the values obtained are recalculated to mole fraction PTMG, y, by the calibration expression for IR results

$$y = 0.1008 + 1.5873(A(2850)/A(1735)), \tag{10}$$

where the methylene absorption at 2850 cm^{-1} was normalized with respect to the carbonyl absorption at 1735 cm^{-1}, and the expression for ESCA results

$$\text{C/O} = (6 - 2y)/(4 - 3y), \tag{11}$$

where the carbon/oxygen atom ratio was measured, the mol% PTMG was found to be higher on the surface than in the bulk, as shown in Table 10 (Fig. 14). The surface enrichment of PTMG in the PES/PTMG fibers is consistent with the behavior shown by a segmented polyether-urethane [14] and the excess of polyether on Biomer surfaces [15].

The mol% PTMG on the surface seems, however, to be independent of the composition in the bulk since the values are almost constant within the range studied. The layer enriched in PTMG is hydrophobic, and it seems to protect the underlying PES, which is more sensitive toward hydrolytic degradation.

TABLE 10. Fraction of PTMG in the Surface of PES/PTMG Fibers[a]

Sample	Mol%, bulk	Mol%, MIR-FTIR	Mol%, ESCA
A	19.9	40.4	59.9, 63.2, 67.0
B	32.9	50.8	61.8, 63.2
C	34.0	53.5	–
D	42.6	57.9	–
E	54.0	45.1	62.3, 62.3, 70.0
F	58.7	31.5	62.7, 68.5

[a] Results of analysis by ESCA and MIR-FTIR are recalculated to mol% PTMG by using the corresponding calibration curves.

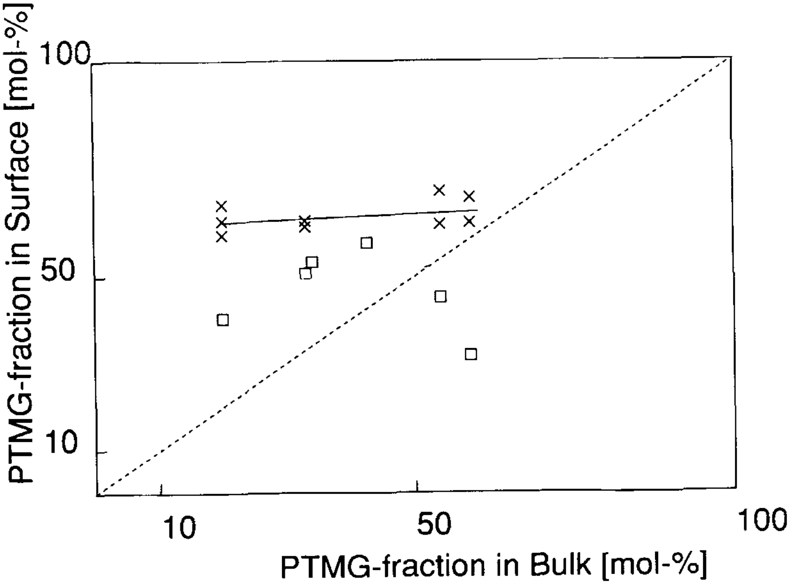


FIG. 14. The PTMG fraction in the surface of PES/PTMG fibers calculated from IR and ESCA data plotted against the mol% PTMG of the fibers. □ = IR and X = ESCA.

The clue to the mechanism of degradation of these materials may lie in the data from the IR and ^{1}H-NMR studies of the degraded fibers. Sample F here displays the most predominant change in properties with increasing degradation time. Figures 5 and 6 show a minimum in the methylene fraction on the 46th day, followed by a slow increase until the 87th day, after which the methylene fraction decreases again.

The following mechanism is proposed: The methylene fraction decreases initially (Figs. 5 and 6), indicating that the layer enriched in PTMG is washed away. Then water diffuses into the amorphous part of the polyester, and the ester linkages in the tie-chains between the amorphous polyether and the crystalline polyester are slowly hydrolyzed. The polyester then slowly leaves the fiber, and this leads to an increase in the methylene fraction, as shown in Figs. 5 and 6.

The rate of degradation is now dependent on the molecular weight and on the crystallinity of the polyester and, therefore, the fiber with the lowest crystallinity of the polyester block (F) degrades most rapidly. When this happens the mechanical properties of the material deteriorate (see Figs. 1 and 2) since the connection between the low molecular weight polyether chains and the polyester crystallites is broken. The remaining oligomeric ester chains become incorporated in the crystalline structure, resulting in an increase in the heat of fusion, as shown in Fig. 4.

In Sample F, which contains the largest amount of the polyether, the polyester part is of lower molecular weight and the crystallinity is less than in Samples A and E. The loss of mechanical strength is thus more rapid when the protecting polyether layer is eroded.

According to this theory, all the PES/PTMG fibers should be almost unaffected by hydrolytic degradation up to a point where the PES is reached. The subsequent degradation behavior should then be dependent on the crystallinity of the PES block. The theory describes the observed behavior of the sample containing 50 mol% PTMG, but the degradation time of 172 d was too short for this behavior to be observed for the samples containing 20 and 54 mol% PTMG.

CONCLUSIONS

The elastic fibers of block copolymer had a surface concentration of PTMG that was higher than the bulk concentration and independent of the bulk concentration within the range studied. The molecular weight of the PES blocks is a function of the mole fraction of PTMG and decreases inversely as the fraction increases.

These thermoplastic elastomers PES/PTMG degrade slowly *in vitro* by a combined erosion and hydrolysis mechanism, whereas PES/PEG seemed to degrade by hydrolysis of the bulk material as well as of the surface. The rate of degradation was most rapid for the sample having the highest mole fraction of polyether. The tensile strength remained almost unchanged for a considerable period before decreasing rapidly to 0.

At the point where the tensile strength of the polymers is lost, the molecular weight decreases and the heat of fusion increases as the result of the hydrolytic attack on the tie-chains. The higher the mole fraction of polyether, the lower is the crystallinity, and low crystallinity makes the block copolymers more sensitive toward water.

This behavior makes the PES/PTMG materials interesting as long-term degradable sutures with elastic properties. Further tests are, however, necessary to optimize the fiber composition to give a suitable degradation time and elasticity and to compare the degradation mechanism *in vivo* with the results of the *in vitro* tests described in this paper.

ACKNOWLEDGMENTS

This work is supported by The Swedish Board for Technical Development. We wish to express our gratitude to Maria Pålsson, who performed the ESCA measurements, and to Henrik Kereszty for carrying out the SEM studies.

REFERENCES

[1] D. K. Gilding, in *Biocompatibility of Clinical Implant Materials,* Vol. 2, (D. F. Williams, ed.), CRC Press, Boca Raton, Florida, 1981, pp. 209-232.

[2] E. J. Frazza and E. E. Schmitt, *J. Biomed. Mater. Res. Symp., 1,* 43 (1971).

[3] A. K. Schneider, U.S. Patent 3,636,956 (1972).

[4] N. Doddi, C. C. Versfeldt, and D. Wasserman, U.S. Patent 4,052,988 (1977).

[5] D. J. Casey and M. S. Roby, European Patent 0 098,394 (1984).

[6] A.-C. Albertsson and O. Ljungquist, *J. Macromol. Sci.–Chem., A23,* 393 (1986).

[7] A.-C. Albertsson and O. Ljungquist, *Ibid., A23,* 411 (1986).

[8] A. Fradet and E. Maréchal, *Eur. Polym. J., 14,* 749 (1978); (a) *Ibid., 14,* 755 (1978); (b) *Ibid., 14,* 761 (1978).

[9] A.-C. Albertsson and O. Ljungquist, *J. Macromol. Sci.–Chem., A24,* 977 (1987).
[10] H. R. Dickinson, A. Hiltner, D. F. Gibbons, and J. M. Andersson, *J. Biomed. Mater. Res., 15,* 577 (1981).
[11] A.-C. Albertsson and S. Karlsson, *J. Appl. Polym. Sci.,* In Press.
[12] K. Makino, H. Ohsima, and T. Kondo, *J. Microencapsulation, 3*(3), 203 (1986).
[13] A. Hult and B. Rånby, *Polym. Degrad. Stab., 8,* 89 (1984).
[14] A. K. Sha'aban, S. McCartney, N. Patel, I. Yilgor, J. S. Riffle, D. W. Dwight, and J. E. McGrath, *ACS Polym. Prepr., 24*(2), 130 (1983).
[15] R. W. Paynter, B. D. Ratner, and H. R. Thomas, *Ibid., 24*(1), 13 (1983).

Received March 26, 1987
Revision received October 28, 1987