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

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To cite this Article Albertsson, Ann-Christine and Ljungquist, Olle(1987) 'Degradable Polymers. III. Synthesis and Characterization of Aliphatic Thermoplastic Block Copolyesters', Journal of Macromolecular Science, Part A, 24: 8, 977 — 990

To link to this Article: DOI: 10.1080/00222338708076930

URL: http://dx.doi.org/10.1080/00222338708076930

J. MACROMOL. SCI.—CHEM., A24(8), pp. 977-990 (1987)

DEGRADABLE POLYMERS. III. SYNTHESIS AND CHARACTERIZATION OF ALIPHATIC THERMOPLASTIC BLOCK COPOLYESTERS

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ABSTRACT

A group of new block copolymers has been synthesized and characterized. The copolyesters were step-polymerized with six different polyether feeds, ranging from 21.1 to 53.3 mol%. The resulting poly(ethylene succinate)-*b*-poly(tetramethylene glycol) (PES/PTMG) polymers were characterized by GPC, DSC, IR, and NMR, and tensile strength measurements were performed. The molar composition of the polymers was determined by NMR and also correlated with IR. The compositions of the polymers agree well with those expected from the composition of the feed. Fibers for tensile strength measurements were extruded, and samples for dynamic mechanical tests (DMTA) were compression molded. The crystallinity, the melting temperature, the fiber strength, and the elastic bending modulus decreased with increasing polyether content, whereas the breaking strain increased.

INTRODUCTION

In our series on degradable stiff polymers [1] and elastomers [2], we have now synthesized a block copolymer of an aliphatic polyester, poly(ethylene succinate), and an aliphatic polyether, poly(tetramethylene glycol). These materials are thermoplastic elastomers and may be processed by conventional techniques (i.e., fiber extrusion or injection molding).

Materials that are similar to human tissue with respect to tensile strength and elasticity have interesting potential uses in surgery [3]. Biodegradable devices are especially advantageous since the need for a second operation for removal is eliminated. Degradable block copolyesters of the aromatic polyester, poly(ethylene terephthalate) with poly(oxyalkenes), poly(ethylene glycol) [4], or poly(tetramethylene glycol) [5] have been reported in the literature. The use of poly(tetramethylene glycol) instead of poly(ethylene glycol) increased elasticity and hydrophobicity, which in turn led to slower hydrolytic degradation. One drawback of these materials, however, is that on degradation, they leave aromatic oligomers within the human body long after they have degraded mechanically.

Aliphatic block copolymers that degrade rapidly (within 10 days) have been made previously [6]. However, our goal is to synthesize polymers with a slower rate of degradation. For this study we have chosen the polymer described here instead of the copolymer based on poly(glycolic acid).

The hydrophobicity and the melting point are increased, compared to the polyester containing poly(ethylene glycol) [2], and the effects on the properties of the material are reported in this paper.

EXPERIMENTAL

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.

Synthesis

The reagents (dimethyl succinate (0.30 mol, 43.85 g), ethylene glycol (0.387 mol, 24.02 g), poly(tetramethylene glycol)), and the thermal stabilizer (phenothiazine, 0.001 mol, 0.2 g) were added to a carefully dried 3-necked kettle. Nitrogen was bubbled for a minimum of 15 min during rapid stirring, and the catalyst (tetraisopropyl titanate, 0.5 mL) was added. The temperature was then raised to 150°C, and this condition was held until the condensation slowed. Vacuum was applied by replacing the combined distilling head and nitrogen inlet with a vacuum line. The pressure was slowly lowered to <50 Pa (0.5 mbar). The temperature was then raised to 180°C, and this condition was maintained overnight or until the product was too viscous to stir. The resulting off-white viscous product was dissolved in dichloromethane and precipitated by dripping into methanol.

Prototype Production

Fibers for tensile strength measurements were extruded at 20°C above the melting temperature (T_{peak}) in a small lab-scale extruder made in our workshop. The die had a diameter of 0.5 mm, and the internal volume of the extruder was 5 mL. The fibers were then allowed to cool to room temperature and crystallize. The time for the material to crystallize was dependent on the amount of polyether. The fibers containing 19.9 mol% polyether crystallized in 3-5 min whereas those containing 58.7 mol% took 4-6 h to crystallize. These fibers were then cold-drawn (necked) at room temperature to produce the oriented fibers which were used in the tensile tests. The fibers produced in this way had diameters of 0.30 ± 0.07 mm, except Sample 2 which was 0.40 ± 0.05 mm.

The extruder mentioned above was also used to melt and degas the polymers when samples for the dynamic mechanical tests (DMTA) were compression molded. The melt was placed in the mold (2 X 6 X 15 mm) at room temperature and allowed to cool and crystallize as above, but under 6 tons pressure.

Polymer Characterization

The resulting block copolymers, poly(ethylene succinate)-*b*-poly(tetramethylene glycol) (PES/PTMG), were characterized by GPC, DSC, IR, and NMR, and tensile strength measurements were performed. Triplicate samples were used for tensile tests and DSC analysis. A Waters 6000 A pump with two Shodex columns (GPC AC-80M/S) connected to a differential refractometer was used for GPC with chloroform as the solvent, and the flow rate was 1 mL/min. The apparatus was run at 28°C with the solvent pressure at 4.55 MPa (650 psi). Polystyrene standards were used for calibration. The apparatus used for DSC was a Perkin-Elmer DSC-2 with a heating rate of 10°C/min. The sample weight was 5 mg.

The FTIR used was a Perkin-Elmer 1710, the samples were films on NaCl windows. The NMR was a JEOL JNM-PMX 60 SI. Samples were dissolved in deuterochloroform. Tensile strength was measured with an Instron 1122 equipped with pneumatic grips (No. 2714-002). A Polymer Laboratories DTMA was used for determination of the elastic moduli and tan δ. The samples described above were examined at 1 Hz with a heating rate of 4°C/min.

RESULTS AND DISCUSSION

Results of Synthesis

The block copolymer was step-polymerized with six different polyether feeds, ranging from 21.1 to 53.3 mol% (Table 1). This interval was chosen because of the results described previously [2] for polyethylene glycol at 44.4 mol%. All of the polymerizations yielded products capable of forming fibers. Since one potential application of these materials is as sutures in surgery, their ability to form fibers is of crucial importance. From the GPC measurements it seems that the threshold number-average molecular weight (polystyrene units) for ability to form fibers is about 20 000. Materials with a higher content of poly(tetramethylene glycol) were also polymerized but did not meet this demand. The yields in this one-step polymerization ranged from 74.1 to 95.7% with one exception (2) of 63.6%. This somewhat

TABLE 1. Synthesis Results

Sample	PTMG in feed, mol%	Yield, wt%	$\overline{M}_n^{PS}$
1	53.3	74.1	36 600
2	47.8	63.6	45 600
3	21.1	95.7	28 800
4	43.1	89.1	35 700
5	38.0	89.2	31 600
6	32.7	88.4	24 700

lower yield is probably due to monomers or low oligomers distilling off during the evacuation at the end of the polymerization.

Results of NMR and IR Analysis

The molar composition of the polymers was determined by NMR. The integrated peaks at 4.3 and 3.5 ppm (Fig. 1) corresponding to the polyester hydrogens and the polyether hydrogens, respectively, (A and B in Formula 1) and their relative intensities were used to calculate the composition (Table 2).

The compositions of the polymers agree well with those expected from the feed composition. Only the sample with the lowest yield (2) has a higher PTMG content. This is probably due to the decrease of the polyester content caused by evaporation of the succinate esters, while the polyether content remains intact.

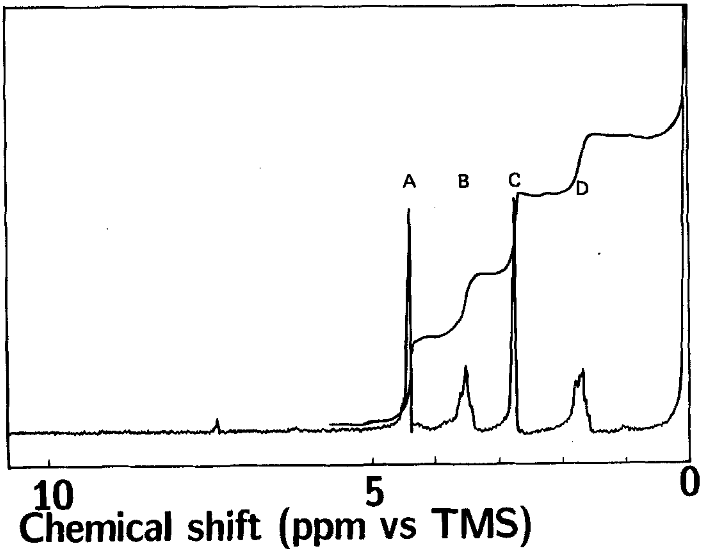

FIG. 1. 60 MHz ^{1}H-NMR spectrum of PES/PTMG. Peaks labeled A and B are used for the determination of mol% PTMG. Peak assignments:

$+COCH_2CH_2COOCH_2CH_2O+$ $+CH_2CH_2CH_2CH_2O+$

C C A A B D D B

TABLE 2. Results of NMR and IR Analysis

	PTMG				
Sample	In feed, mol%	In polymer, mol%	$I_{3.5\text{ppm}}$	$I_{4.3\text{ppm}}$	$\frac{A_{2855}}{A_{1735}}$
1	53.3	54.0	34	29	0.2266
2	47.8	58.7	44	31	0.2522
3	21.1	19.9	09	37	0.0619
4	43.1	42.6	29	39	0.1367
5	38.0	34.0	24	47	0.1054
6	32.7	32.9	24	49	0.0847

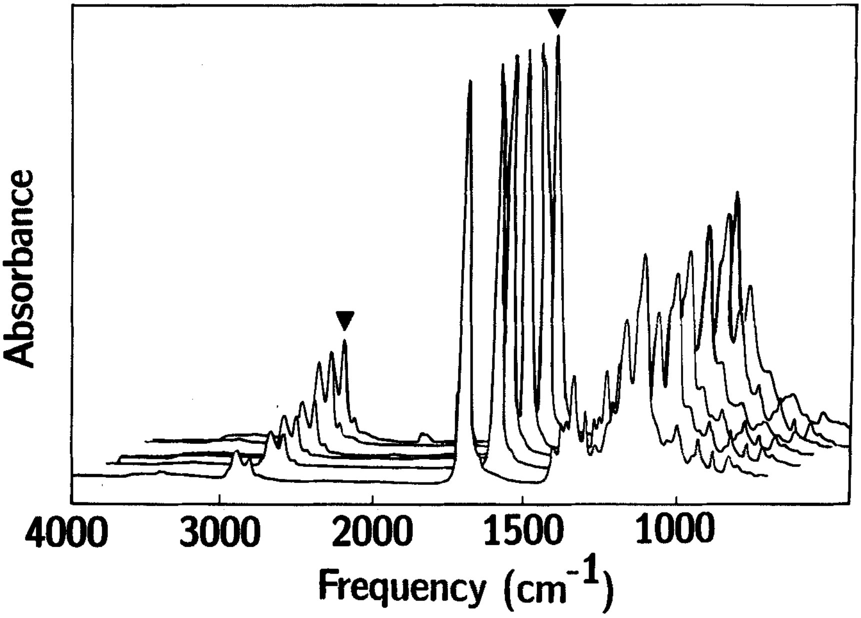

FIG. 2. Infrared spectra of PES/PTMG. Labeled peaks are used for correlation test of NMR.

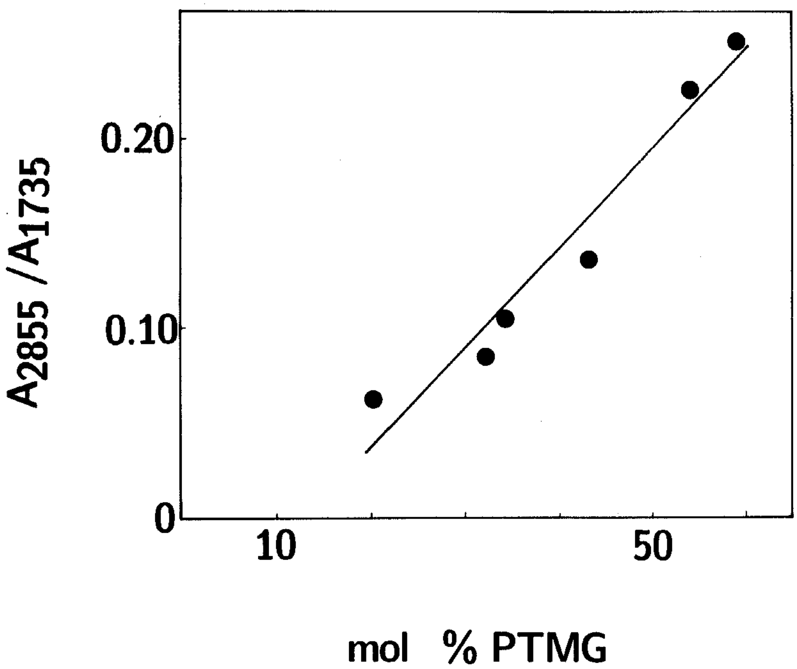

FIG. 3. Correlation between infrared absorption at 2855 cm^{-1} (relative to 1735 cm^{-1}) and mol% PTMG as determined by NMR intensities at 3.5 ppm (relative to 4.3 ppm).

The infrared absorption of methylene groups at 2855 cm^{-1} relative to the ester absorption at 1735 cm^{-1} (Fig. 2) is plotted versus the NMR integrals in Fig. 3. The correlation coefficient according to the least square method is 0.972. The molar composition as determined by NMR is used throughout this paper as a description of the materials.

Results of DSC Analysis

A typical thermogram is shown in Fig. 4. The area under the peak melting at the highest temperature (corresponding to the polyester block) is used to calculate the heat of fusion (ΔH_f) which is plotted versus mol% polyether in Fig. 5. The straight line drawn, has a correlation coefficient of 0.968 and an intercept of 64.4 J/g (15.4 cal/g), excluding the point indicated in parentheses.

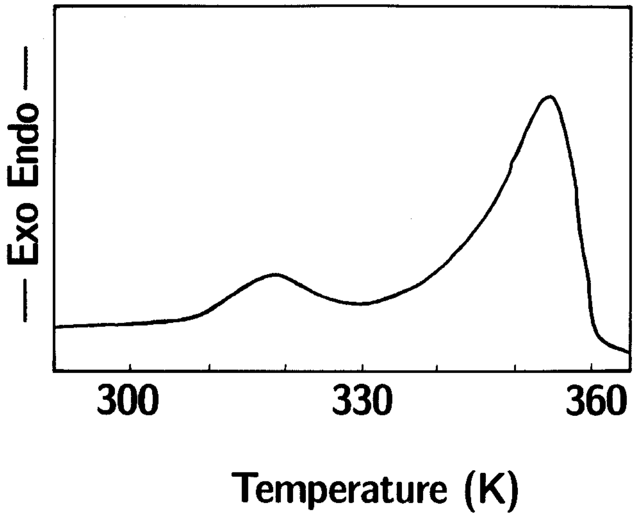

FIG. 4. DSC scan of PES/PTMG.

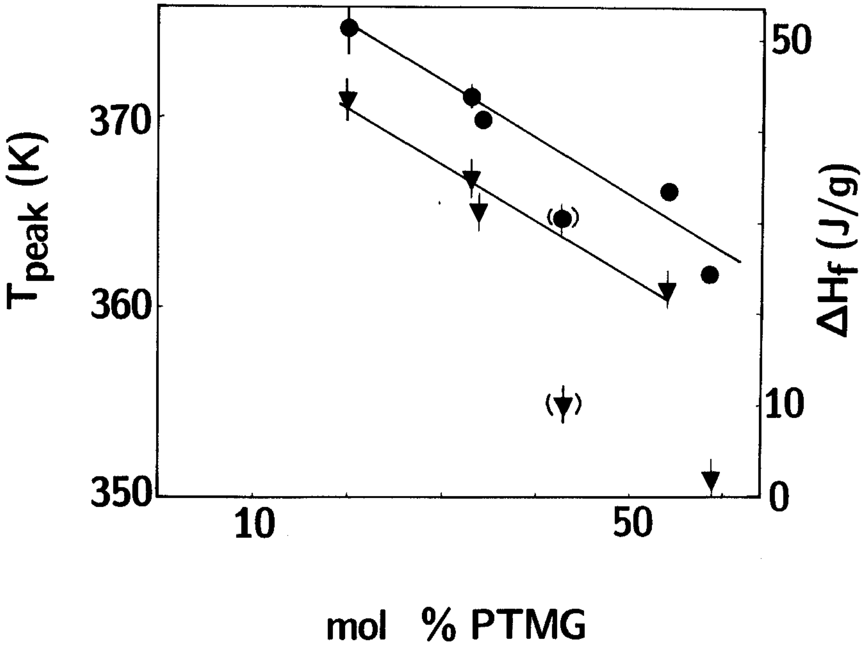

FIG. 5. The heat of fusion (ΔH_f) (●) and the melting temperature (T_{peak}) (▼) plotted versus the mol% PTMG.

This intercept represents the heat of fusion of the homopolymer in this surrounding and gives a crystallinity of 58.5% when compared to ΔH_f^0 of 110 J/g [7]. The melting temperature, T_{peak}, decreases with increasing polyether content from 371 K (98°C) at 19.9 mol% to 351 K (78°C) at 58.7 mol%. The small peak at 310-320 K (37-47°C) is only present in the oriented fibers. It disappears when the fibers are melted and it is not present in the undrawn materials. The transition could be due to a stress-induced crystallization of the polyether chains, taking place when the fibers are cold-drawn. The extensively studied aromatic block copolymer, poly(hexamethylene therephthalate)/poly(oxytetramethylene) [8], has been investigated by SAXS. The diffraction pattern of a material extended to 300% of its original length shows spots that indicate the presence of crystalline polyether. These patterns disappeared when the materials was heated at 60°C [9].

Mechanical Properties

Tensile strength measurements were used to investigate mechanical properties, such as the breaking stress, σ_b, and the breaking strain, ϵ_b, of the oriented fibers. These properties are plotted versus the mol% polyether in Fig. 6, and it can be seen that the breaking stress decreases linearly with increasing polyether content. The correlation coefficient is 0.994, and the slope is -1.59 MPa/mol%, excluding the sample in parentheses. This indicates that the polyester matrix is responsible for the fiber strength and elongation. This behavior was also observed in the aromatic system poly(ethylene terephthalate)/poly(tetramethylene glycol) [10]. The breaking strain, calculated as $(l_b - l_0)/l_0$, remained at 200% from 19.9 to 58.7 mol% polyether, at which point it increase to 500%. The elastic modulus in bending, E', as determined by DMTA, for the samples is plotted versus temperature in Fig. 7. All the samples have essentially the same modulus at low temperature (-100°C), but as the temperature increases, differences become apparent. The higher the polyether content, the lower the temperature needed to start the decline of the modulus. This phenomenon was also found in the investigation of the loss factor, tan δ; the transition starts earlier and the peak grows larger as the polyether content increases (Fig. 8). The differences still persist after the transition—the higher the polyether content, the lower the modulus, as expected. The modulus at 37°C and the tan δ are given in Table 3 and plotted versus polyether content in Fig. 9.

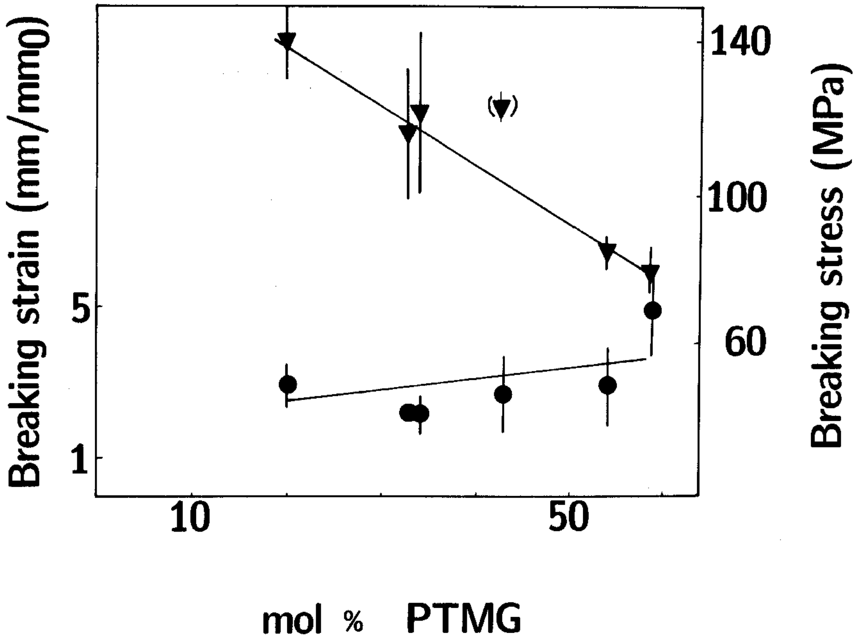

FIG. 6. Breaking stress, σ_b (▼), and breaking strain, ϵ_b (●), plotted versus mol % PTMG.

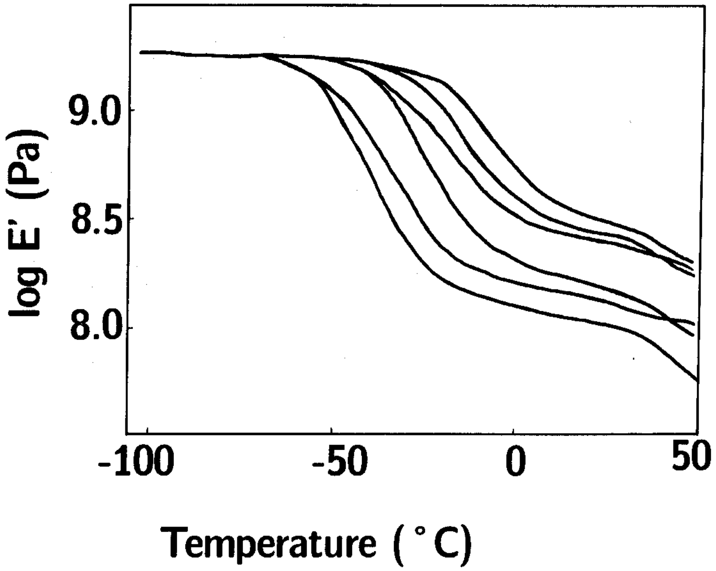

FIG. 7. Log E' at 1 Hz plotted versus temperature. The mol % PTMG increases from top to bottom.

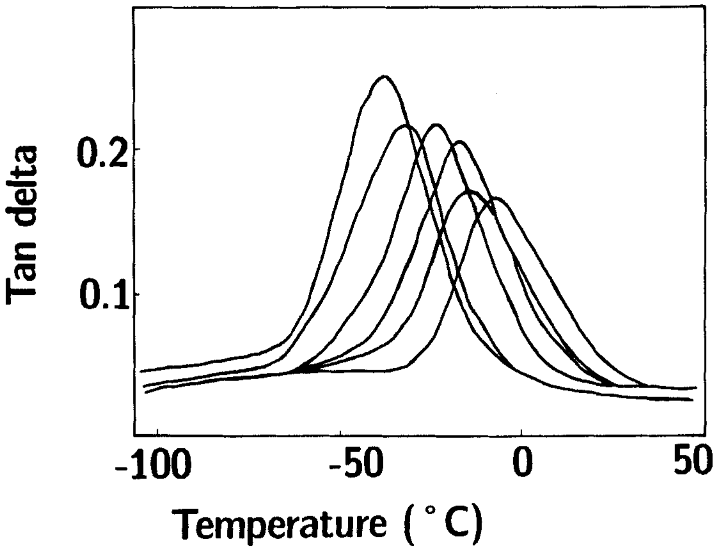

FIG. 8. Tan δ at 1 Hz plotted versus temperature. The mol % PTMG increases from right to left.

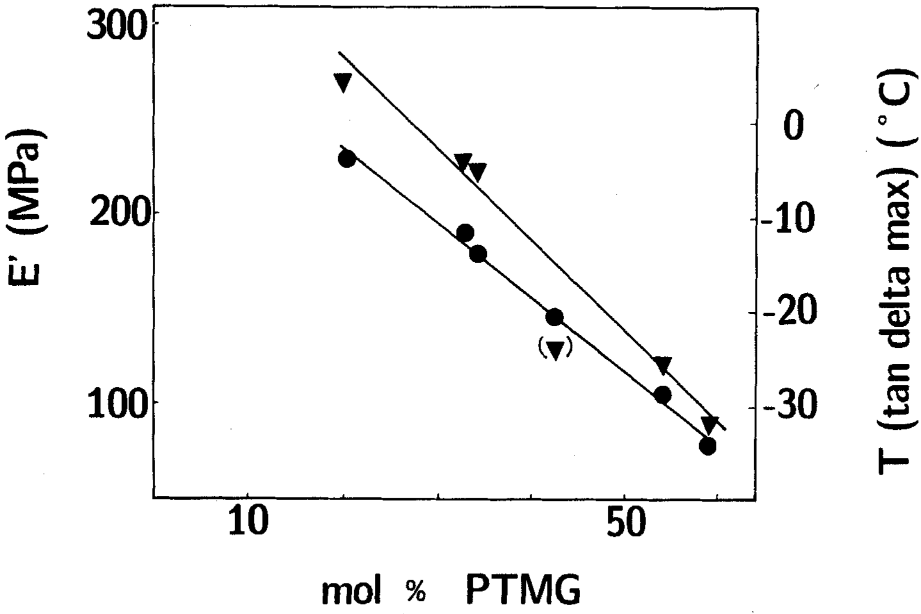

FIG. 9. E' modulus at 37°C (▼) and the temperature for the tan δ maximum (●) plotted versus mol % PTMG.

TABLE 3. Results of DSC and Mechanical Tests

Sample	ΔH_f, J/g	T_{peak}, K	σ_b, MPa	ϵ_b	E', MPa	$T(\tan \delta_{\max})$, °C
1	34.3 ± 0.5	361	084 ± 04	2.9 ± 1.2	121.0	-29
2	24.3 ± 0.5	351	079 ± 06	4.9 ± 1.0	086.5	-34
3	51.6 ± 2.5	371	140 ± 10	2.3 ± 0.6	268.5	-04
4	30.7 ± 1.6	355	123 ± 04	2.7 ± 1.0	130.9	-21
5	41.7 ± 0.7	365	121 ± 21	2.2 ± 0.5	223.9	-14
6	44.5 ± 1.2	367	116 ± 18	2.3[a]	228.0	-12

[a] One sample.

CONCLUSIONS

A group of new block copolymers, which to our knowledge has not been previously reported in the literature, has been synthesized and characterized. These aliphatic poly(tetramethylene glycol)-*b*-poly(ethylene succinate) polymers are thermoplastic elastomers with interesting properties. The mechanical properties of the synthesized block copolymer can be varied with respect to the elastic modulus in bending as well as the breaking stress and strain in tensile load by changing the content of the polyether. These polymers belong to the group of materials which contain hydrolyzable bonds and could be suitable for the construction of degradable devices for use in surgery. Some of the prototypes described are undergoing hydrolytic degradation tests, and we hope to report the results in the near future.

ACKNOWLEDGMENT

This work was supported by the Swedish Board for Technical Development (STU).

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Received September 18, 1986
Revision received November 25, 1986