

Synthesis and Characterization of Biodegradable Aliphatic Copolyesters with Poly(tetramethylene oxide) Soft Segments

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ABSTRACT: A series of aliphatic poly(ether-ester)s based on flexible poly(tetramethylene oxide) (PTMO) and hard poly(butylene succinate) (PBS) segments were synthesized by the catalyzed two-step transesterification reaction of dimethyl succinate, 1,4-butanediol, and α,ω -hydroxy-terminated PTMO ($M_n = 1000$ g/mol) in the bulk. The content of soft PTMO segments in the polymer chains was varied from 10 to 50 mass %. The effect of the introduction of the soft segments on the structure, thermal, and physical properties, as well as on the biodegradation properties was investigated. The composition and structure of the aliphatic segmented copolyesters were determined by ^1H NMR spectroscopy. The molecular weights of the polyesters were verified by viscometry of dilute solutions and polymer melts. The thermal properties were investigated

using DSC. The degree of crystallinity was determined by means of DSC and WAXS. Biodegradation of the synthesized copolyesters, estimated in enzymatic degradation tests on polymer films in phosphate buffer solution with *Candida rugosa* lipase at 37°C, was compared with hydrolytic degradation in the buffer solution. Viscosity measurements confirmed that there was no change in molecular weight of the copolyesters leading to the conclusion that the degradation mechanism of poly(ether-ester)s based on PTMO segments occurs through the surface erosion. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1777–1786, 2007

Key words: poly(ether-ester)s; poly(tetramethylene oxide); polycondensation; biodegradable; enzymes

INTRODUCTION

The application of biodegradable polymers for packing, sanitary, and agricultural purposes instead of bioresistant polymers is one way to diminish the problem of environment pollution by plastic waste. Aliphatic polyesters have been recognized as one of the most promising biodegradable materials because they are readily susceptible to biological attack and their degradation products, the starting diols and acids or hydroxy acids, are nontoxic and can enter the metabolic cycles of bioorganisms.^{1–3} Aliphatic polyesters, such as poly(glycolic acid) (PGA), poly(L-lactic acid) (PLLA), poly(ϵ -caprolactone) (PLC), and different poly(β -hydroxyalkanoates) and poly(ω -hydroxyalkanoates), have already found biomedical application and are commercially available.

Aliphatic polyesters from diacids and diols poly(alkylene dicarboxylate) of high molecular weight were successfully synthesized using highly effective transesterification catalysts and the vacuum tech-

nique^{4,5} as well as their chain extension with diisocyanates. A broader use of synthetic aliphatic polyesters derived from diacids and diols is limited by their low melting temperatures and relatively poor mechanical properties. Poly(butylene succinate) (PBS) is the most investigated biodegradable aliphatic polyesters because it is one of the few aliphatic polyesters with a melting temperature above 100°C. This polyester and its copolyesters with ethylene glycol and adipic acid are commercially available under the tradename *Bionolle*.⁶ Because of the poor thermal properties of aliphatic polyesters, great interest has been given to research on aliphatic-aromatic copolyesters, which are designed to combine the biodegradability of the aliphatic units with the beneficial physical properties of the aromatic units.^{7,8} For example, poly(butylene adipate-co-butylene terephthalate) is a commercial product marketed under the trade name *Ecoflex* (BASF). Its biodegradation behavior and properties have been reported by Müller and coworkers.^{9,10} However, with the introduction of aromatic units, the biodegradation properties deteriorated. Among all factors that can affect biodegradability,^{11–16} the hydrophilicity–hydrophobicity balance is the one that can be easily directed by the chemical structure and composition of the repeating units. The biodegradable properties of polyesters can be improved by increasing the hydrophilicity. One

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of the ways of modifying the properties of polyesters is the introduction of hydrophilic segments, such as polyethers, into the backbone of the polymer chains. The introduction of polyether soft segments into copolyesters leads to the formation of segmented polymers, the mechanical properties of which can be easily controlled by the type, the weight percent, and the length of the soft segments.

The first attempt to increase biodegradability by increasing the hydrophilicity of materials by the introduction of soft segments was performed with aromatic polyesters.¹⁷⁻¹⁹ The results showed that the biodegradation of these segmented polyesters is controlled not only by water absorption but also by the concentration of biodegradable ester linkages between the different segments. This approach was broadened to the investigation of the aliphatic-aromatic biodegradable polyesters with either poly(ethylene oxide) (PEO) or poly(tetramethylene oxide) (PTMO) as a constituent part of hydrophilic soft segment.^{20,21}

There are only few reports on pure aliphatic segmented copolyesters, such as that of Albertsson and Ljungquist²² concerning poly(ethylene succinate) with 8.3 mol % of PEG having a molecular weight around 400. Nagata et al.²³ synthesized PBS copolymers containing PEO with molecular weights in the range from 200 to 2000 and reported that with increasing the content of PEO, the hydrolysis rate of the copolymers increased, but their melting temperatures and degrees of crystallinity decreased. Also, the tensile strength and elongation were significantly reduced in the presence of the hydrophilic PEO segments. Other polyesters based on poly(ethylene succinate), L-lactic acid,²⁴ and PEO were also investigated. For example, copolyesters based on ϵ -caprolactone and PEO have found some special biomedical applications.²⁵ The biodegradability properties were improved, as expected, in all polymers in which PEO was incorporated. However, the oxidative instability of materials containing PEO under ambient conditions and exposure of these polymers to daylight are problems that have to be overcome.

PTMO is also used as soft segments in the synthesis of thermoplastic copolyester elastomers and it is more stable than PEO. At the same time, PTMO possesses hydrophilic groups and can improve the biodegradability of hydrophobic aliphatic polyesters. Although used in an attempt to modify the biodegradability properties of aromatic polyesters,¹⁷⁻²⁰ to the best of our knowledge, there have been no reports on the synthesis and characterization of pure aliphatic poly(ether-ester)s with PTMO as the soft segments.

In a previous study, the synthesis and characterization of two series of aliphatic poly(ether-ester)s

modified with two different types of soft segments, i.e., PEO and PTMO of the same molecular weight but different hydrophilicity, were reported.²⁶ The results obtained in the biodegradation tests with polymers with only 10 mass % of soft segments showed that the introduction of the hydrophilic polyether segments increased the biodegradability and was a good way to tailor the biodegradability of aliphatic polyesters. In this article, the synthesis, structure, and properties of segmented polyesters modified with a relatively high level of PTMO segments, varying between 10 and 50 mass %, are presented. The modification of the synthetic procedure allowed the preparation of these poly(ether-ester)s with higher contents of PTMO segments, the molecular weights of which were such as to provide for good mechanical properties and good filmability. This enabled besides the structural and physical properties also the biodegradability of these poly(ether-ester)s with higher PTMO contents to be investigated. The polymer films were subjected to enzymatic attack by lipase from *Candida rugosa*, and the enzymatic as well as hydrolytic degradation were evaluated from the weight loss of the polymers.

EXPERIMENTAL

Materials

Dimethyl succinate (Aldrich) was used as received. α,ω -Hydroxy terminated PTMO with a molecular weight of 1000 g/mol (Fluka) was used as obtained. 1,4-Butanediol was purified by vacuum distillation. Titanium-tetrabutoxide ($\text{Ti}(\text{OBu})_4$; Aldrich) was used as a solution in dry *n*-butanol (1 : 9 v/v). *C. rugosa* lipase was purchased from Sigma.

Synthesis of poly(ether-ester)s

The aliphatic copolyesters were synthesized by a two-step transesterification reaction in the bulk, starting from dimethyl succinate, 1,4-butanediol, and α,ω -hydroxy-terminated PTMO ($M_n = 1000$ g/mol). The diol component was used in a 15 mol % excess over the dimethyl ester. As an example, the synthesis of a poly(ether-ester) with 10 mass % of PTMO is described. A three-necked laboratory reactor equipped with a condenser, nitrogen inlet tube, magnetic stirrer, and thermometer was charged with 40.30 g (0.276 mol) of dimethyl succinate, 4.24 g (0.0043 mol) of PTMO, and 28.07 g (0.312 mol) of 1,4-butanediol. The reaction mixture was purged with nitrogen, and the reaction was started by the introduction of 0.09 g (0.265 mmol) of $\text{Ti}(\text{OBu})_4$ as catalyst. The reaction mixture was heated quickly to 150°C and gradually (10°C per 10 min) to the final reaction temperature of 220°C. The methanol formed

during the first stage was distilled off. The methanol was collected in a yield of around 63–67%. The second phase of reaction was carried out with a second portion of catalyst (0.265 mmol), under vacuum ($p = 0.5$ mmHg), and the reaction mixture was maintained under these conditions for 6 h. After the completion of the reaction, the copolyester was cooled in the reactor to room temperature under nitrogen without precipitation. All the other poly(ether-ester)s were synthesized in the manner described earlier. The amount of the PTMO was varied so as to obtain poly(ether-ester)s with 10, 20, 30, 40, and 50 mass % of soft segments.

Characterization of poly(ether-ester)s

^1H NMR (200 MHz) spectra were recorded in CDCl_3 solution with tetramethylsilane as the reference standard, using a Varian-Gemini-200 Instrument. The ^1H NMR spectra of these polymers showed characteristic peaks: protons from succinic acid moieties at $\delta = 2.63$ ppm, methylene protons from PTMO attached to the ester group and ether group at $\delta = 4.09$ – 4.23 ppm and $\delta = 3.39$ – 3.44 ppm, respectively, and protons from the central and terminal methylene groups of 1,4-butanediol residues at $\delta = 1.62$ – 1.71 ppm and $\delta = 4.09$ – 4.12 ppm, respectively. The compositions of the polyesters were calculated from the relative intensities of the peaks characteristic for the succinic acid moieties and the peaks of methylene protons next to the ether bond from PTMO.

The viscosities of dilute solutions of the polymers in chloroform were measured at 25°C using an Ubbelohde viscometer. The intrinsic viscosity (η) was calculated from these measurements.

Differential scanning calorimetry (DSC) was performed using a PerkinElmer Pyris 6 DSC analyser under nitrogen atmosphere in the temperature range from -50 to 150°C at a heating and cooling rate of $10^\circ\text{C}/\text{min}$. The polyester samples were scanned from 30 to 150°C , then cooled to -50°C , and heated again to 150°C . The melting temperatures were determined from the initial scan as the temperatures of the main endothermic peak in the DSC curves. The glass transition temperatures were calculated from the DSC scans as the middle point of the heat capacity change.

A 951 TGA Thermogravimetric Analyzer (TA Instruments) was used for the thermogravimetric measurements. Nonisothermal experiments were performed in the temperature range 40 – 600°C at a heating rate of $10^\circ\text{C}/\text{min}$. The thermal stability of the polyesters was studied under a dynamic atmosphere of helium (flow rate $70\text{ cm}^3/\text{min}$). The average weights of the samples were ~ 7 mg.

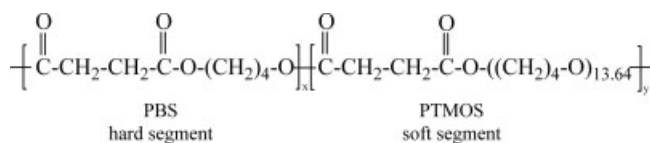
Complex dynamic viscosity (η^*) was measured on polymer pellets using a Rheometrics RMS-605 Instrument, operating in the dynamic mode at 120°C . The frequency was varied from 0.1 to 100 rad/s. The radius of the samples was 25 mm, and the thickness was about 1.5 mm. The polyester pellets were prepared by press molding from the melt at about 150°C .

Wide-angle X-ray scattering (WAXS) measurements of copolymer films were performed using a Siemens D500 diffractometer with $\text{Cu K}\alpha$ Ni-filtered radiation, in the 2θ range from 10° to 30° at a scan speed of $0.02^\circ/\text{s}$. The degree of crystallinity was calculated using a basic method for the differentiation between crystalline and amorphous scattering in the X-ray diffraction scans. The ratio of the area under the crystalline peaks to the total (amorphous and crystalline) area gives the degree of crystallinity.

Enzymatic degradation tests were performed on copolyester films. The polymer films were obtained by hot pressing at 20°C above the melting temperature. In addition, the films were stored at ambient temperature at least 3 weeks before characterization to reach equilibrium crystallinity, which was then evaluated by WAXS measurements. The films ($10 \times 40\text{ mm}^2$ and about $200\text{-}\mu\text{m}$ thick) were incubated in a phosphate buffer solution ($\text{pH} = 7.00 \pm 0.01$) in the presence of lipase from *C. rugosa* in a water bath at 37°C . Enzymatic degradation tests of the polyesters films were run in duplicate. The enzyme concentration was 2.0 mg/mL , and for every 7 days, the enzyme solution was replaced with a freshly prepared one. Simultaneously, blank experiments in the phosphate buffer solution without the enzyme were carried out. The films were removed either from the enzymatic or from the buffer solution after selected time intervals, washed with distilled water, and dried under vacuum at room temperature to constant weight. The extent of biodegradation was quantified as the weight loss divided by the initial sample surface area.

RESULTS AND DISCUSSION

A series of high molecular weight poly(ether-ester)s (PBSTMO) based on soft PTMO and hard PBS segments was synthesized using a two-step transesterification reaction in the bulk. The amount of PTMO soft segments in the poly(ether-ester) chains was varied between 10 and 50 mass %. The first step, or transesterification reaction, was carried out in the temperature range 150 – 220°C under atmospheric pressure with a 15% stoichiometric excess of 1,4-butanediol. The syntheses were carried out with a highly effective catalyst, tetra-*n*-butyl-titanate, without the addition of a heat stabilizer. In the second



Scheme 1 Structural formula of the poly(ether-ester)s, PBSTMOs.

step, the reaction was carried out by maintaining the reaction mixture at 220°C for 6 h under vacuum to remove the excess 1,4-butanediol and, hence, produce chain extension. All the synthesized poly(ether-ester)s were isolated by cooling to room temperature under nitrogen atmosphere without precipitation. The structural formula of the synthesized segmented aliphatic poly(ether-ester)s based on succinic acid is shown in Scheme 1.

The composition and structure of the poly(ether-ester)s

The ^1H NMR spectrum of the poly(ether-ester) with 10 mass % soft segments, PBSTMO 10, is shown in Figure 1. Because of the overlapping of the methylene protons from the two diol components, which comprise different segments, i.e., the butanediol and PTMO moieties, the composition could be calculated only by comparing the content of one diol with the total number of acid moieties. The poly(ether-ester) compositions were determined from the ^1H NMR spectra as the relative intensities of the proton peaks from the methylene groups attached to the ether oxygen from the PTMO (d) (3.39–3.44 ppm) and of the succinate repeating unit (a) (2.63 ppm). Thus, the mole fraction of soft PTMO segments was calculated, using the formula:

$$y(\text{soft segment, mol \%}) = \frac{I_d/N_d}{I_a/N_a}$$

where I_d and I_a are the intensities of the corresponding peaks, and $N_a = 4$, and $N_d = 50.56$ are the numbers of protons in the corresponding units.

The ^1H NMR analysis confirmed that succinic moieties are incorporated into polymer chains in the hard as well as in the soft segments. The theoretical and experimental mass % and mol % composition of the soft segments of the synthesized poly(ether-ester)s are presented in Table I. These results show that the soft segments were incorporated into the poly(ether-ester)s in amounts, which were slightly in excess of that to be expected from the compositions of the starting reaction mixtures. For all the samples, except for PBSTMO 20, the excess was in the range of experimental error. It could be concluded that the composition of the poly(ether-ester)s was in good agreement with those expected from the composition of the feed, except for PBSTMO 20.

In addition to hydrophilicity, another important parameter, which determines the biodegradability potential of poly(ether-ester)s, is the average number of degradable ester linkages connecting two different segments in the copolymer chains. The average length of hard PBS segments is in inverse correlation with the number of degradable ester linkages in the polymer chain, which are connected to the soft segments. The average length of the hard PBS segments was calculated from the mole fraction of PBS in the copolymer assuming random copolymerization of the comonomers, using the following formula:

$$L_n = \frac{1}{1 - x_{\text{PBS}}} - 1$$

The results summarized in Table I show that the average degree of polymerization of PBS was between 6 and 55, indicating a decrease in the length of the hard segments with the increase in the content of soft PTMO segments.

The composition of the starting reaction mixture, as well as that of the poly(ether-ester)s, the intrinsic viscosities, and the complex dynamic viscosities of the polymer melts at 120°C are given in Table II.

The intrinsic viscosities of the synthesized polyesters were between 67.2 and 93.7 cm^3/g for the copolyesters and 180.3 cm^3/g for the homopolyester, PBS. The values of the intrinsic viscosities of synthesized copolyesters and PBS are considerably higher than those reported in a previous work.²⁶ The higher vacuum and better mixing of the reaction mixture compared to those in the previous work resulted in these higher viscosity values. Both the higher vacuum and better mixing of the reaction mixture pro-

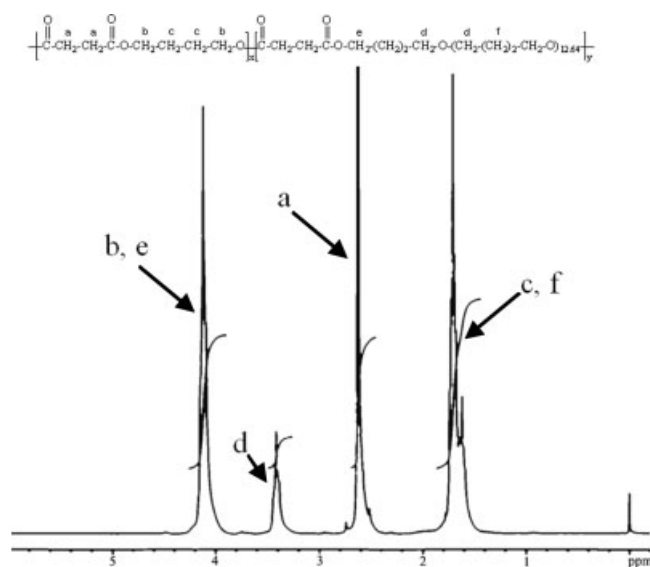


Figure 1 ^1H NMR spectrum of the polyester with 10 mass % of poly(tetramethylene oxide), PBSTMO-10.

TABLE I
Composition and Average Length of the Hard Segments of the Synthesized Poly(ether-ester)s

Polymer	Mass fraction of soft segments (mass %)		Mole fraction of soft segments (mol %)		L_n
	Theoretical	Experimental	Theoretical	Experimental	
PBSTMO 10	10	10.5	1.7	1.8	55
PBSTMO 20	20	22.3	3.8	4.3	22
PBSTMO 30	30	31.8	6.4	6.9	13
PBSTMO 40	40	41.4	9.6	10.1	9
PBSTMO 50	50	50.2	13.7	13.8	6

mote diol elimination as well as chain extension in the second step of the transesterification reaction. Also, these results are in agreement with the fact that the reaction rate decreases with the increase in the content of PTMO soft segments due to the higher transesterification activation energy of PTMO compared to 1,4-butanediol.^{21,27} Therefore, to obtain copolyesters with higher contents of soft PTMO segments and with higher molecular weights, the extent of the reaction should be increased through prolonging the duration of the polycondensation. Simultaneously, the increase of soft polyether molar content decreases the melt viscosity of the reaction mixture, thus facilitating the elimination of the by-products and favorizing the formation of polymer with higher molecular weights, such as in the case of the sample PBSTMO 50.

The values of the Newtonian complex dynamic viscosity (η^*) at 120°C, which could be used as an indicator of the molecular weight of poly(ether-ester)s were in the range from 3 to 70 Pa s (Table II) and were one decade lower compared to aliphatic polyester, PBS. The complex dynamic viscosity was also influenced by the increased flexibility of poly(ether-ester) chains and because of this the values do not follow the trend in molecular weight change in the series.

In this study, it was shown that relatively high-molecular weight poly(ether-ester)s can be synthe-

sized at 220°C using a highly effective catalyst, such as tetra-*n*-butyl-titanate, without a heat stabilizer. The copolymers exhibited macromolecular behavior and were suitable for the preparation of flexible and tough films by the melt-pressed method.

As reported previously, poly(ether-ester)s suffer from low stability if exposed to light under ambient conditions. Also, in the present case, polymer samples that were stored in the form of slices and thin films, a change in color was observed after storage for 6 months. A decrease in the intrinsic viscosities in the range from 2.5 to 27.6% (the values are given in Table II) was observed as a result of exposure to light in the absence of an antioxidant. Thus, extreme caution is necessary during the storage of these polymers, i.e., they should be kept in the dark at low temperatures. Also, to prevent the degradation of the poly(ether-ester)s under daylight condition, vitamin E or some other hindered phenol derivatives, which are able to scavenge radicals,¹⁹ could be used.

Thermal properties of poly(ether-ester)s

The synthesized poly(ether-ester)s were partly crystalline polymers, for which melting and glass transition temperatures were observed by DSC analysis. The DSC thermograms of the synthesized poly(ether-ester)s recorded during heating and cooling

TABLE II
Composition of the Reaction Mixture, Composition, Intrinsic Viscosity, and Complex Dynamic Viscosity of the Poly(ether-ester)s

Polymer	Composition of reaction mixture (BS/PTMOS) ^a	Composition of copolyester (BS/PTMOS) ^b	$[\eta]$ (cm ³ /g; after 6 months) ^c	η^* (Pa s) 120°C, 1 Hz
PBS	100/0	100/0	180.3	754
PBSTMO 10	90/10	89.5/10.5	81.9 (71.3)	69
PBSTMO 20	80/20	77.7/22.3	67.2 (65.6)	40
PBSTMO 30	70/30	68.2/31.8	76.9 (55.7)	3
PBSTMO 40	60/40	58.6/41.4	76.2 (67.4)	5
PBSTMO 50	50/50	49.8/50.2	93.7 (87.5)	29

^a BS, weight fraction of butylene succinate units; PTMOS, weight fraction of poly(tetramethylene oxide) succinate units.

^b Determined by ¹H NMR spectroscopy.

^c Determined after 6 months of exposure to daylight at room temperature.

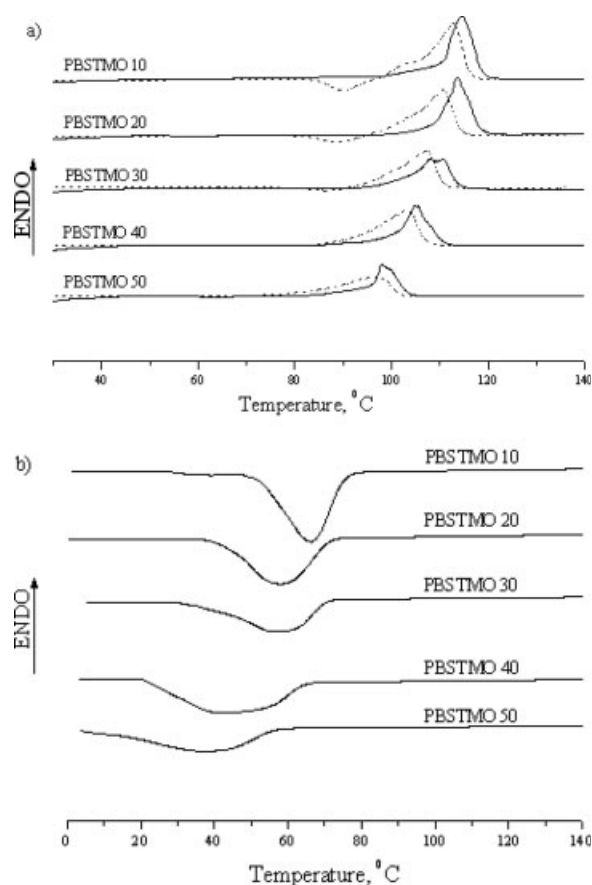


Figure 2 DSC thermograms of the aliphatic poly(ether-ester)s with different contents of soft segments in the polymer chain a) heating rate 10°C/min (— first heating, ---- second heating), b) cooling rate 10°C/min.

are presented in Figure 2(a,b), respectively. Only one peak, corresponding to the melting of the hard PBS phase, was observed in the DSC scans, showing that the second component does not crystallize and is mostly incorporated in the amorphous domains. In the thermograms of the second heating run, multiple endothermic peaks were observed. This behavior can be explained by the melt-crystallization model, which was reported earlier for PBS and its copolyesters,^{28,29} and by the presence of crystallites of different size and perfection, due to the irregularity of the

length of the PBS segments in the poly(ether-ester)s. The results obtained from DSC analysis, the melting temperature (T_m), the enthalpy of melting (ΔH_m), the crystallization temperature (T_c), the glass transition temperature (T_g), and the degree of crystallinity of the poly(ether-ester)s and, for the sake of comparison, of PBS homopolymer are given in Table III.

The melting temperature was determined as the temperature of the main peak in the DSC curve from the first run. The melting temperatures shift to lower temperatures with increasing fraction of soft segments from 116°C (PBS) to 98°C (PBSTMO 50), which is the expected behavior of the copolymers. However, the melting temperatures of all the synthesized poly(ether-ester)s, except for the one with the highest amount of PTMO, are above 100°C, which is important for the potential application of these biodegradable copolymers. Unlike the melting temperatures, the crystallization temperatures are much more affected by the introduction of the soft PTMO segments into the copolymer chains, showing hindered crystallization of the copolymers compared to the homopolymer. The difference in the melting and crystallization temperature (supercooling) ($\Delta T_h = T_m - T_c$) is an indication of the rate of crystallization of different polymers. PBS, which is considered to be a fast crystallizing polymer, has a ΔT_h value of 40°C. The ΔT_h values for the hard segments of the synthesized aliphatic poly(ether-ester)s lie in the range from 49 and 58°C, indicating that the rate of crystallization decreases with the increase in the content of soft segments. Practically, this means that the copolymers reach their equilibrium degree of crystallinity slower, which should be taken into consideration during the design of experiments when a dependence on the degree of crystallinity is expected, as is the case with biodegradability.

The enthalpies of melting, ΔH_m , were determined from the area of the melting thermograms and from the obtained values, the corresponding degrees of crystallinity were calculated, as the ratio of the apparent ΔH_m and the enthalpy of melting of perfectly crystalline PBS. Because of the copolymerization and increase in the noncrystallizing component, the

TABLE III
Thermal Properties and Degree of Crystallinity of the Synthesized Polymers

Polymer	T_m (°C)	ΔH_m (J/g)	T_c (°C)	T_g (°C)	X_c (%) ^a DSC	$X_{c\text{-PBS}}$ (%) DSC	X_c (%) ^b WAXS
PBS	116	84.5	75	-36	76.5	76.5	53.0
PBSTMO 10	115	66.1	66	-38	59.8	65.2	52.8
PBSTMO 20	114	57.0	58	-38	51.6	64.5	45.3
PBSTMO 30	111	49.7	57	-38	45.0	61.9	40.7
PBSTMO 40	105	39.6	47	-46	35.8	59.0	35.6
PBSTMO 50	98	32.2	40	-38	29.1	59.7	33.3

^a Calculated by dividing the observed heat of fusion by the theoretical value calculated on the basis of the group contribution.

^b The degree of crystallinity was determined by the X-ray method.

expected decrease in the enthalpy of melting as well as in the corresponding degrees of crystallinity was observed for poly(ether-ester)s. The total degree of crystallinity of the poly(ether-ester)s (X_c) was in the range 29.1 to 59.8%, i.e., lower than the degree of crystallinity of the homopolymer (PBS) (76.5%), and decreased proportionally with the increase in the content of PTMO segments. The degree of crystallinity of the crystallizing component alone, i.e., PBS, was calculated by means of the following equation:

$$X_{c\text{PBS}} = \frac{\Delta H_m}{\Delta H_m^0 w_{\text{PBS}}}$$

where ΔH_m^0 is the theoretical value of the enthalpy of melting of perfectly crystalline PBS homopolymer, calculated on the basis of the group contribution method³⁰ (110.5 J/g), and w_{PBS} is the weight fraction of hard segments (crystallizing component) in the sample, determined by ¹H NMR spectroscopy. The degrees of crystallinity of the hard PBS segments in the poly(ether-ester)s were in the range 59–65%, which is lower than the degree of crystallinity of the homopolymer PBS. It was also observed that the values of $X_{c\text{PBS}}$ tended to decrease with the increase in the content of soft PTMO segments, from which it can be concluded that the presence of the soft segments disturbs the crystal growth of the PBS hard segments. Thus, the reason for the observed decrease of the X_c of the poly(ether-ester)s is caused not only by the decrease in the amount of the crystallizing component but is also affected by the hindered crystallization of the hard phase. The values of the degree of crystallinity obtained indicate that the poly(ether-ester)s should be more prone to biodegradation, since it was shown in a number of studies that this is one of the most important factors determining the biodegradability behavior.^{9,11}

All the synthesized poly(ether-ester)s showed only one glass transition temperature, which is due to the transition occurring in the noncrystalline phase of the sample consisting of a mixture of the soft segments and noncrystallized PBS hard segments. The glass transition temperature varies slightly with the composition of the copolyesters. PBS homopolymer has a glass transition temperature of -36°C , which is higher than the T_g values of the poly(ether-ester)s, indicating the mixing of the amorphous phase of the hard PBS segments with the soft PTMO segments.

X-ray analysis of poly(ether-ester)s

Since on the one hand the degree of crystallinity is a very important factor determining the biodegradability of polymers and on the other hand the terminal treatment can affect the physical properties of the

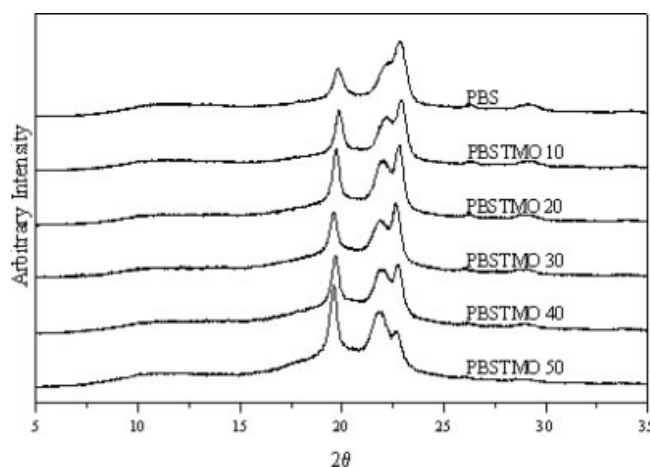


Figure 3 X-ray diffractograms of the poly(ether-ester)s with different contents of soft segments.

polymer films, it is important to have information on the degree of crystallinity of the samples prepared for the actual biodegradability test. X-ray analysis of the polymer films prepared for the enzymatic degradation study was performed to obtain further information on the crystalline structure and degree of crystallinity of these samples. The diffraction diagrams for the PBS homopolymer and the poly(ether-ester)s with different contents of PTMO soft segments are shown in Figure 3. Characteristic peaks for PBS appear at $2\theta = 19.81^\circ, 22.18^\circ, 22.84^\circ, 26.29^\circ,$ and 29.15° . An electron diffraction study revealed that the PBS crystallites have a monoclinic crystal lattice, as was reported earlier³¹: $a = 0.523$ nm, $b = 0.908$ nm, $c = 1.079$ nm, and $\beta = 123.87^\circ$. The characteristic peaks for the copolyester with the highest content of soft segments are at $2\theta = 19.59^\circ, 21.83^\circ, 22.65^\circ, 26.00^\circ,$ and 28.80° . With the increase in the content of soft segments, the peak at $2\theta = 21.83^\circ$ is more pronounced. The positions of the peaks in the diffractograms of the copolyesters show that there is no change in the type of the crystal lattice characteristic for PBS homopolymer and that aliphatic poly(ether-ester)s crystallites have a monoclinic crystal lattice similar to that of PBS. With increasing the content of soft segment in the polymers, the peaks of these copolymers are shifted toward lower values of 2θ , indicating a small increase in the unit cell dimensions.

The degrees of crystallinity of the synthesized poly(ether-ester)s were in the range from 33 to 53%, as determined from the WAXS measurements (Table III), which are lower than the values obtained from the DSC measurements (29–60%). This can be explained as a consequence of possible distortions in the crystal lattice. The trend in the degree of crystallinity of the poly(ether-ester) films in the series was the same as already observed for the native polymer

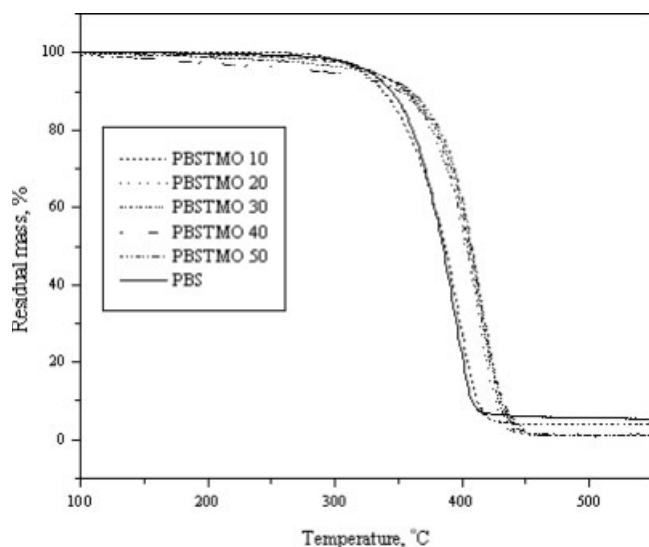


Figure 4 TG curves for the poly(ether-ester)s and PBS-homopolymer under a dynamic helium atmosphere, heating rate $10^\circ/\text{min}$.

in the DSC measurements. All copolymers have lower crystallinity than the homopolymer, which decreases with the increase in the amount of soft PTMO segments.

Thermogravimetric analysis of poly(ether-ester)s

The thermal stability of aliphatic polyesters is an important parameter, which could limit their application. The thermal stability of the synthesized poly(ether-ester)s was studied by nonisothermal thermogravimetry (TG) under helium atmosphere. The TG curves of the synthesized polyesters with different contents of flexible segments are shown in Figure 4. From the shape of the TG curves, it can be observed that the thermal behaviors of PBS and the poly(ether-ester) modified with 10 mass % of flexible polyether segments are very similar and quite different in thermal stability to all the other copolymers.

For the sake of quantification, the characteristic temperatures for weight losses of 5, 50, and 90%, $T_{5\%}$, $T_{50\%}$, $T_{90\%}$, respectively, as well as the residual weight at 550°C in helium are given in Table IV. The $T_{5\%}$ value is considered to represent the beginning of thermal degradation. The degradation of the polymers commences between 321 and 331°C , except for the sample PBSTMO 40 with 40 mass % of soft PTMO segments, the degradation of which starts at 294°C . The values of $T_{50\%}$ and $T_{90\%}$ in the series increased with the increase in the content of soft PTMO segments. Although the degradation of the copolymers starts at lower temperatures, according to the shape of the TG curves and the corresponding $T_{50\%}$ values, the copolymers with higher amounts of soft segments are more stable than the homopolymer

TABLE IV
TGA Data (Temperature of 5, 50, and 90% weight loss and residue at 550°C)

Polymer	$T_{5\%}$ ($^\circ\text{C}$)	$T_{50\%}$ ($^\circ\text{C}$)	$T_{90\%}$ ($^\circ\text{C}$)	Residue at 550°C (mass %)
PBS	327	385	408	5.4
PBSTMO 10	321	386	412	4.2
PBSTMO 20	331	402	426	1.4
PBSTMO 30	330	406	429	1.2
PBSTMO 40	294	404	432	0.9
PBSTMO 50	327	407	431	1.31

and poly(ether-ester) with the lowest amounts of soft segments. The residual mass of the poly(ether-ester)s at 550°C increased from 0.9 to 4.2% (5.4% for PBS homopolymer) with increasing weight fraction of PBS segments. From these results, it could be concluded that the residual mass in helium originated mainly from the PBS fraction.

Hydrolytic and enzymatic degradation of poly(ether-ester)s

To investigate the effect of the structure of the aliphatic poly(ether-ester)s on biodegradation, enzymatic degradation tests were performed with *C. rugosa* lipase at 37°C in phosphate buffer solution for 4 weeks. The biodegradability of the copolyesters was determined by monitoring the weight loss of the polyesters films divided by the total surface area with time. The normalized weight losses of the polyester samples after degradation for 7 days in buffer solution both with lipase (enzymatic degradation) and without lipase (hydrolytic degradation) are presented in Figure 5 as a function of the content of the

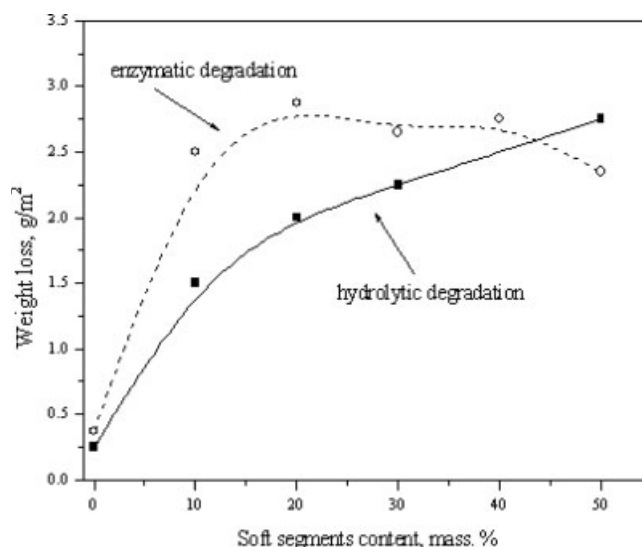


Figure 5 Normalized weight losses of the poly(ether-ester)s with different contents of soft segments degraded for 7 days in buffer solution both with and without lipase.

soft PTMO segments. The weight losses of the homopolymer PBS samples in the enzymatic and blank tests are almost the same. Thus, the presence of the enzyme does not catalyze the degradation of PBS. In the absence of lipase, the weight loss due to hydrolytic degradation increases with the increase in the content of soft PTMO segments in the polymer chains from 0.25 g/m² for PBS to 2.75 g/m² for PBSTMO 50. As can be seen, all the copolymers with hydrophilic soft PTMO segments show higher weight losses in both types of degradation experiments, compared to the PBS homopolymer. This increase in erosive degradation of the poly(ether-ester)s can be explained by the increased flexibility of copolymer chains due to the presence of the soft PTMO segments and, therefore, by the decrease in the crystallinity.

Incorporation of the PTMO soft segments leads to an increase in the hydrolytic degradability of the copolymers, which increased steadily with the increase in the content of soft segments. On the other hand, incorporation of just 10 mass % of soft segments results in a large increase in degree of enzymatic degradation. The biodegradability then remains almost constant in the investigated range of the content of soft segments incorporated into the polymer chains. The weight loss in the enzymatic degradation tests of the copolymers containing soft PTMO segments in the range from 10 to 30% was slightly higher (0.4–1.0 g/m²) compared to hydrolytic degradation. Whereas for the polyesters with higher contents of PTMO segments (PBSTMO 40 and PBSTMO 50), the enzymatic degradation was within experimental error at same level as the hydrolytic degradation. The hindered biodegradation of these two copolymers could be the consequence of the hard PBS segments containing an insufficient number of degradable ester bonds for the catalytic enzyme action. According to the results given by Hercog et al.,³² the enzymatic degradation rate of aliphatic copolyesters in the presence of lipase depends mainly on the availability of the active center of the lipases, which is located inside protein and, therefore, the chain must be able to reach the catalytic active center. It has been reported that each molecule of lipase cover ~ 70–90 ester bonds. The capability of the bonds to reach the active center is assumed to depend mainly on the polymer chain flexibility. In the case of poly(ether-ester)s, this idea could be extended to include not only dependence on chain mobility but also on the dimension of the hard PBS segments. The results of enzymatic degradation confirmed that the poly(ether-ester)s with a degree of polymerization of the hard segments in the range of 55–13 (PBSTMO 10, –20, and –30), each containing two ester bonds in the PBS repeating units, could be more available to catalytic action than the poly-

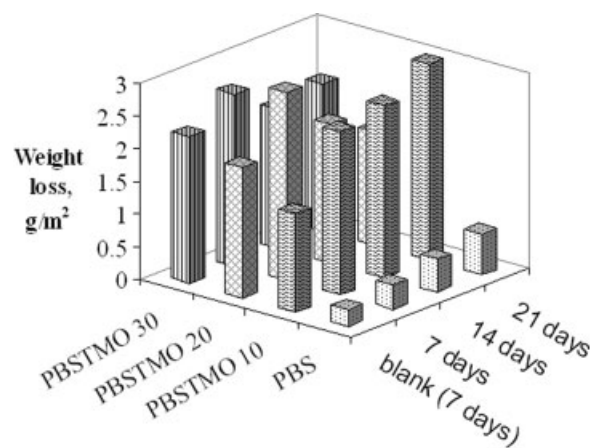


Figure 6 Normalized weight losses of the aliphatic poly(ether-ester)s in the enzymatic degradation tests with *Candida rugosa* lipase.

(ether-ester)s with the higher contents of PTMO segments and shorter PBS segments (PBSTMO 40 and –50).

The samples of poly(ether-ester)s after exposure for 7 days to hydrolytic and enzymatic degradation were analyzed by dilute solution viscosimetry. Measurements of the inherent viscosity confirmed that there was no change in the molecular weight of the residual polymers. This means that the enzymatic and hydrolytic degradation are the consequence of surface erosion and not of bulk degradation.

To gain more insight into the degradation behavior of the poly(ether-ester)s, the enzymatic degradation was followed with time for the homopolymer PBS and the copolymers PBSTMO 10, –20, and –30. Some film samples of PBSTMO 40 and PBSTMO 50 partially disintegrated into smaller fragments after 3 weeks of incubation in the buffer solution and thus the results of the degradation are presented only for the other polymers. The results of enzymatic degradation of the poly(ether-ester)s and PBS during 3 weeks of exposure to the enzyme and of hydrolytic degradation obtained in the blank tests (without the addition of the enzyme and carried out for 7 days) are shown in Figure 6. For all investigated times, the degradability is higher for the poly(ether-ester)s compared with that of PBS. This increase in erosion degradation of the copolymers can be explained by the increased flexibility of the copolymer chains due to the presence of the soft polyether PTMO segments and, therefore, the decrease in the crystallinity. Degradation is also affected by the hydrophilicity/hydrophobicity balance and is usually initiated in the amorphous domains. The present results confirm, as has been reported, that the degradation of segmented copolymer films is influenced by the concentration of degradable ester linkages between the hard segments and the soft polyether segments.²²

Under the employed experimental conditions, the amount of degradation of PBSTMO 20 and PBSTMO 30 is only slightly higher in the presence of the enzyme. However, in the cases of PBS and PBSTMO 10, there was an increase in degradation with time and a significant increase in the weight loss in the presence of the lipase.

The results of the hydrolytic and enzymatic degradation of the samples showed that the introduction of soft PTMO segments up to 50 mass % into the polymer chains increased the degradability compared to PBS in the examined period of 4 weeks.

CONCLUSIONS

High molecular weight aliphatic poly(ether-ester)s based on succinic acid and PTMO were successfully synthesized by a catalyzed transesterification reaction in the melt. The composition of the poly(ether-ester)s, obtained on the basis of ^1H NMR spectra analysis, showed that the content of soft segments in the copolymers was close to the composition of the feed.

The melting temperatures of the poly(ether-ester)s were lower than that of PBS and decreased with the increase in the content of soft segments. However, except for the copolymer with 50 mass % of PTMO segments, all other poly(ether-ester)s had melting temperatures above 100°C , which is important for their possible application. The copolymers exhibited macromolecular behavior and were suitable for the preparation of flexible and tough films by the melt-pressed method.

The total degree of crystallinity of the poly(ester-ether)s was in the range of 29.1–59.8%, i.e., lower than the degree of crystallinity of the homopolyester (PBS) (76.5%) and decreased with the increase in content of PTMO segments. The degree of crystallinity (X_{CPBS}) calculated with respect to the weight fraction of PBS segments in the poly(ether-ester)s indicated a decreasing tendency of crystallization of the hard segments with the increase in the content of soft PTMO segments. The X-ray diffraction analysis performed on the copolymer films prepared for the biodegradability tests confirmed the trend of decreased crystallinity in the series as observed by DSC measurements of the native polymers. The X-ray diffraction patterns indicated that in the poly(ester-ether)s the hard phase PBS crystallized in a monoclinic crystal lattice, i.e., similar to PBS, but with a small increase in the unit cell dimensions.

Hydrolytic and enzymatic degradation in the presence of *C. rugosa* showed that the introduction of soft PTMO segments into the polymer chains increased the degradability compared to PBS in the

examined period of 4 weeks. The poly(ether-ester)s show promise as biodegradable elastomers, especially the samples containing 10–30 mass % of soft segments, which have satisfying thermal properties and simultaneously good biodegradability.

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