

Synthesis and characterization of biodegradable aliphatic copolyesters with hydrophilic soft segments

DANIJELA JOVANOVIĆ, MARIJA S. NIKOLIĆ[#] and JASNA DJONLAGIĆ^{*#}

Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia and Montenegro (e-mail: jasna@tmf.bg.ac.yu)

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Abstract: In this study, the synthesis, structure and physical properties of two series of segmented poly(ester-ether)s based on poly(butylene succinate) and two different types of polyethers were investigated. The poly(ester-ether)s were synthesized by transesterification reaction of dimethyl succinate, 1,4-butanediol and poly(ethylene oxide) (PEO, $M_n = 1000$ g/mol) in the first series, and poly(tetramethylene oxide) (PTMO, $M_n = 1000$ g/mol) in the second. The mass fraction of soft segments was varied between 10 and 50 mass. %. The effect of the introduction of two different polyether soft segments on the structure, thermal and rheological properties were investigated. The composition of the poly(ester-ether)s, determined from their $^1\text{H-NMR}$ spectra, showed that incorporation of soft polyether segments was successfully performed by the transesterification reaction in bulk. The molecular weight was estimated from solution viscosity measurements and complex dynamic viscosities. The thermal properties investigated by DSC indicated that the presence of soft segments lowers the melting and crystallization temperature of the hard phase, as well as the degree of crystallinity. Dynamical mechanical analysis was used to investigate the influence of composition on the rheological behavior of the segmented poly(ester-ether)s. The results obtained from an enzymatic degradation test performed on some of the synthesized polymers showed that the biodegradability is enhanced with increasing hydrophilicity.

Keywords: poly(ester-ether)s, poly(butylene succinate), poly(ethylene oxide), poly(tetramethylene oxide).

INTRODUCTION

In past decade the interest in the use of biodegradable instead of bioresistant polymers as one solution to solid waste management has grown. The most promising polymers for this application are aliphatic polyesters.¹ Their degradation products, the starting diol and acid, or hydroxy acid are non-toxic and can enter the metabolic cycles of bioorganisms. For this reason they can be defined as potentially

* Corresponding author.

Serbian Chemical Society active member.

environmentally friendly materials. Aliphatic polyesters derived from hydroxy acids, such as poly(lactic acid), and different poly(β -hydroxyalkanoates) and poly(ω -hydroxyalkanoates), have already found application mainly in the field of medicine and are commercially available.²

The difficulties associated with the synthesis of aliphatic polyesters from diacids and diols (poly(alkylene dicarboxylate)) of high molecular weight were recently overcome by the use of highly effective transesterification catalysts and the high vacuum technique.^{3,4} The limiting factor for the broader use of aliphatic polyesters from diacids and diols is their poor thermal properties, *i.e.*, low melting temperatures. One of the few aliphatic polyesters with a melting temperature above 100 °C is poly(butylene succinate), PBS.⁵ This polyester as well as its copolyesters with ethylene glycol and adipic acid are commercially available under the trademark Bionolle. They are highly crystalline polymeric materials with excellent processability on conventional equipment commonly used for the processing of polyolefine.⁶

The biodegradable properties of polyesters can be improved by increasing their hydrophilicity. One way of increasing the hydrophilicity of polyesters is the introduction of hydrophilic segments, such as polyethers, into the backbone of the polymer chains. At the same time, the introduction of polyether soft segments into copolyesters leads to the formation of segmented block polymers, the mechanical properties of which can be easily controlled by the type, the weight percent and length of the soft segments. The first attempts to increase biodegradability by increasing the hydrophilicity of materials were performed with aromatic polyesters.⁷⁻⁹ However, after degradation of the soft segments, there is always the possibility of an aromatic residue remaining which is very resistant to microbial or fungal attack and so can not be degraded under environmental conditions.^{10,11} In order to overcome the problem of the low biodegradability of aromatic polyesters, investigations of segmented aliphatic poly(ether ester amide)s were carried out.¹² There were also attempts to increase the biodegradability of polymers by preparing degradable polyurethanes containing poly(butylene succinate) and poly(ethylene glycol).¹³

The biodegradable aliphatic poly(ester-ether)s investigated so far had poly(ethylene oxide), PEO, as the soft hydrophilic segments. Poly(butylene succinate)¹⁴ and poly(ethylene succinate),¹⁵ as well as polyesters based on L-lactic acid¹⁶ and L-lactic acid in combination with citric acid¹⁷ were investigated. For some special biomedical application, PEO was also used as the soft segment in copolyesters based on ϵ -caprolactone¹⁸ and the microbial polyester poly(*(R)*-3-hydroxybutyrate).¹⁹ In all cases when poly(ethylene oxide) was used, as expected, the biodegradability properties were improved and, depending on the length and content of the polyether, controlled degradable materials could be obtained. However there is still concern because of the oxidative instability of materials containing poly(ethylene oxide) during exposure of these polymers to light under ambient conditions.⁹

Poly(tetramethylene oxide) is more stable than poly(ethylene oxide) and it was shown that aromatic poly(ester-ether)s containing poly(tetramethylene oxide) have improved properties as far as their stability is concerned.⁸ Poly(tetramethylene oxide) is hydrolytically more stable than poly(ethylene oxide). However, poly(tetramethylene oxide) possesses hydrophilic groups and can improve the biodegradability properties of hydrophobic aliphatic polyesters. There were investigations on poly(ester-ether)s containing poly(tetramethylene oxide) based on poly(butylene succinate) and poly(butylene terephthalate)²⁰ but, to the best of our knowledge, there have been no reports on the synthesis and characterization of pure aliphatic poly(ester-ether)s with poly(tetramethylene oxide) as the soft segments.

In this paper the synthesis and characterization of two series of poly(ester-ether)s with different polyethers as soft segments are presented. Two polyethers of the same molecular weight (1000 g/mol) were used for the synthesis: PEO and PTMO. The aim of this study was to investigate the synthesis by transesterification reaction of poly(ester-ether)s, and to establish the effect of polymer composition on the physical properties of the segmented poly(ester-ether)s.

EXPERIMENTAL

Materials

Dimethyl succinate (Aldrich) was used as received. Poly(ethylene oxide), PEO, molecular weight of 1000 g/mol (from Fluka) and poly(tetramethylene oxide), PTMO, of the same molecular weight (Merck) were used as obtained. 1,4-Butanediol was purified by vacuum distillation. Titanium-tetrabutoxide, Ti(OBu)₄, (Aldrich) was used as a solution in dry *n*-butanol (1:9 vol).

Synthesis of polyesters

The copolymers were synthesized by transesterification in the bulk starting from dimethyl succinate, 1,4-butanediol and the corresponding polyether ($M_n = 1000$ g/mol): poly(ethylene oxide)-PEO series and poly(tetramethylene oxide)-PTMO series. 1,4-Butanediol was used in 20 mol% excess over dimethyl succinate. A typical synthesis procedure for a poly(ether-ester) with 10 mass% of soft PEO segments, which was applied for all the other poly(ester-ethers), was as follows: 33.6 g (0.230 mol) of dimethyl succinate, 24.4 g (0.271 mol) of 1,4-butanediol and 4.0 g (4×10^{-3} mol) of poly(ethylene oxide) were placed in a three-necked flask equipped with a magnetic stirrer, a nitrogen introduction tube and a condenser. As the transesterification catalyst, 0.05 g (0.15 mmol) of Ti(OBu)₄ was used. The reaction mixture was purged with nitrogen and heated in the oil bath to 160 °C and then gradually at a rate of 1 °C/min to the final reaction temperature of 220 °C. During this first stage, methanol was distilled off and collected. For the second phase, *i.e.* polycondensation, a second portion of Ti(OBu)₄ (0.15 mmol) was added and vacuum was applied. The reaction mixture was kept under these conditions for 6 h. After completion of the reaction, the resulting product was removed from the reaction flask, dissolved in chloroform and precipitated in a ten-fold amount of cold methanol. The polymer was dried under vacuum at ambient temperature. All the other poly(ester-ether)s were synthesized following the same procedure. The amount of the corresponding polyether was varied so as to obtain segmented poly(ester-ether)s with 10, 20, 30, 40 and 50 mass% of soft segments.

Characterization of the polyesters

¹H-NMR spectra of the polyesters were recorded in CDCl₃ solution with tetramethylsilane as the reference standard using a Varian-Gemini-200 instrument. From the ratio of the integrals of the characteristic peaks in the ¹H-NMR spectra, the compositions of the copolymers were calculated.

The intrinsic viscosities of the copolymers were determined in chloroform using an Ubelodhe viscometer. The measurements were carried out at 25 °C.

Melting temperatures and heats of fusion were determined from differential scanning calorimetry (DSC) measurements that were performed using a Perkin Elmer DSC2 instrument under a nitrogen atmosphere. Poly(ester-ether)s samples (5 mg) were heated, cooled and reheated at a rate of 10 °C/min.

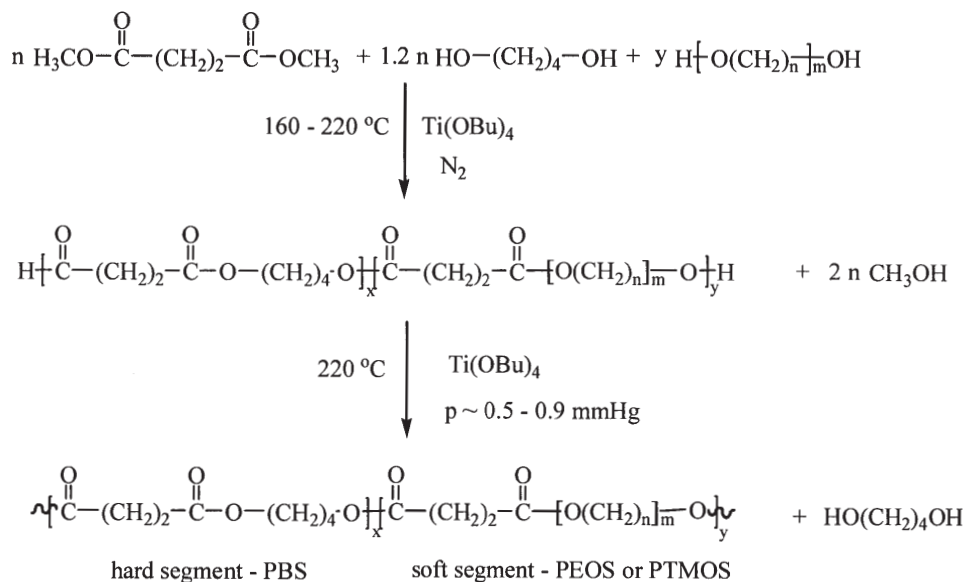
Dynamical mechanical testing was performed on the polyester samples between parallel plates in the rate sweep mode using a Reometrics mechanical spectrometer RMS-605. The measurements were carried out with controlled heating from 80 °C (or 90 °C depending on the sample melting point) to 160 °C. At each temperature, the frequency was changed from 0.1 to 100 rad/s. Polyester pellets (diameter 12.5 mm) were molded from the melt. Also, a PBS sample was analyzed under torsion rectangular conditions on moulded polymer bars (63.0 × 12.4 × 1.0 mm³) over the same temperature range.

Enzymatic degradation tests were performed on poly(ester-ether)s films obtained by hot pressing at 20 °C above the melting temperature. Prior to the enzymatic degradation test, the hot-pressed films (10 × 40 mm² and about 200 μm thick) were aged for three weeks in order to reach equilibrium crystallinity. The poly(ester-ether) films were incubated in a phosphate buffer solution (pH 7.00 ± 0.01) at 37 °C in a presence of *Candida rugosa* lipase (Sigma) at a concentration 1.0 mg/cm³. The enzymatic degradation tests were run in duplicate and simultaneously blank tests without enzyme were carried out. After the predetermined time period (25, 50, 75, 100 and 150 h), the films were removed from the test tubes, washed with distilled water, and dried under vacuum at room temperature to constant weight (reproducibility 0.1 mg). The extent of biodegradation was evaluated as the weight loss divided by the initial sample surface area.

RESULTS AND DISCUSSION

In order to investigate the influence of the content of flexible, hydrophilic segments on the physical properties of biodegradable polyesters, two series of poly(ester-ether)s were synthesized. The poly(ester-ether)s were synthesized by a two-step transesterification reaction in bulk (Scheme 1):

Starting from dimethyl succinate and 1,4-butanediol and an appropriate amount of the required α,ω -hydroxyl terminated polyether, the low molecular weight



Scheme 1.

reaction product methanol was removed in the first phase of the transesterification reaction. After completion of the first phase, vacuum was applied in order to remove the excess 1,4-butanediol and produce chain extension. Removal of the formed methanol is very important in the first phase of the synthesis and so its volume was measured after completion of this stage of the reaction. In order to produce poly(ester-ether)s of high molecular weight, efficient removal of the excess of 1,4-butanediol, which can be achieved with high vacuum, is essential. During the second phase, the vacuum was measured after every hour. The limiting viscosity number, complex dynamic viscosity and yield were determined for each synthesized poly(ester-ether) and the results are summarized in Table I.

TABLE I. The composition of the reaction mixture, yield, limiting viscosity number and complex dynamic viscosity of the synthesized poly(ester-ether)s

Polymer	Composition of the reaction mixture (BS/PEOS or PTMOS)*	Yield/%	$[\eta]/\text{cm}^3\text{g}^{-1}$	η^*/Pas 1 Hz 130 °C
PBS	100/0	–	66.9	86.2
PBSEO-10	90/10	82	118.7	129.9
PBSEO-20	80/20	82	60.5	4.2
PBSEO-30	70/30	87	70.7	20.5
PBSEO-40	60/40	84	31.2	0.2
PBSEO-50	50/50	69	36.6	1.3
PBSTMO-10	90/10	75	64.0	25.9
PBSTMO-20	80/20	85	51.0	7.4
PBSTMO-30	70/30	86	49.6	10.9
PBSTMO-40	60/40	86	58.3	0.2
PBSTMO-50	50/50	82	87.5	4.8

* weight fraction of butylene succinate units – BS, weight fraction of poly(ethylene oxide) (or poly(tetramethylene oxide)) succinate units – PEOS (or PTMOS)

The weight percent of methanol evolved in the first phase of the reaction was above 80 % of the theoretical in all syntheses. $\text{Ti}(\text{O}i\text{Bu})_4$ is obviously a good catalyst for the transesterification reaction, as well as for the second phase of the polycondensation reaction. The yield for almost all the polyesters after precipitation in methanol was 70–87 %. There was a difference in the limiting viscosity number among the polyesters in both series. For the PEO series, the limiting viscosity numbers were in the range from 31.2 to 118.7 cm^3/g , and for the PTMO series from 49.6 to 87.5 cm^3/g . In the PEO series, the higher the soft segments content was, the lower was the limiting viscosity number. This can be a consequence of the smaller hydrodynamic volume of the more flexible macromolecules. This behavior could not be seen in the second series. The limiting viscosity number is in-

fluenced not only by the flexibility of the macromolecular chain but also by the molecular weight and these two effects are superimposed. The low $[\eta]$ for PBSEO-40 and PBSEO-50 can be a consequence of thermal degradation of the polyether during synthesis, because no thermal stabilizer was used. The values of the Newtonian complex viscosity, η^* , at 1 Hz and 130 °C are in the range 0.2 to 129.9 Pas for the PEO series and from 0.2 to 25.9 for the PTMO series. The Newtonian complex viscosity can be used as an indicator of the molecular weight of the poly(ester-ether)s. However, the trends in the limiting viscosity numbers and in the complex viscosity were not the same and the difference in η^* were more pronounced within the series, especially for the PEO series. This can lead to the conclusion that the complex dynamic viscosity is more influenced by the increase in the flexibility of the macromolecular chain than the limiting viscosity numbers. High vacuum in the second phase is very important in order to synthesize polymers of high molecular weight. A clear connection between the applied vacuum and the value of limiting viscosity number could not be established. However, the highest $[\eta]$ obtained for PBSEO-10 was achieved when the applied vacuum was below 0.3 mmHg. In all the other syntheses, the applied vacuum was above 0.4 mmHg and $[\eta]$ did not exceed 100 cm³/g. Filmability of the poly(ester-ether)s from the melt or solution was poor for those poly(ester-ether)s having $[\eta]$ below 60 cm³/g. The obtained results suggest that in order to obtain poly(ester-ether)s with molecular weights high enough to enable good filmability, *i.e.*, mechanical properties, either the applied vacuum must be higher than 0.2 mmHg with a simultaneous shortening of the polycondensation time or a thermal stabilizer for the unstable polyethers must be used during the synthesis.

¹H-NMR analysis of the composition and structure of the poly(ester-ether)s

In order to investigate the molecular structure of the synthesized polyesters, ¹H-NMR analysis was performed. Representative spectra with the corresponding structural formulas are shown in Figs. 1 and 2 for PEO and PTMO based polyesters, respectively.

The composition of poly(ester-ether)s can be calculated comparing the intensities from the diols in the corresponding segments: 1,4-butanediol in the hard segments and polyether in the soft segments. The poly(ester-ether)s composition for the PEO series, content of hard PBS and soft PEOS segments, was determined from the ¹H-NMR spectra as the relative intensities of the proton peaks arising from the butylene moiety (c) and methylene groups attached to the ether oxygen from the polyether moiety (d). The mole fraction of the soft segments was calculated using the formula:

$$x(\text{PBOS segment}), \text{ mol \%} = \frac{I_d / N_d}{I_d / N_d + I_c / N_c}$$

where I_d and I_c are the intensities of the corresponding peaks and $N_c = 4$, and $N_d = 85.27$ are numbers of protons in the corresponding repeating units.

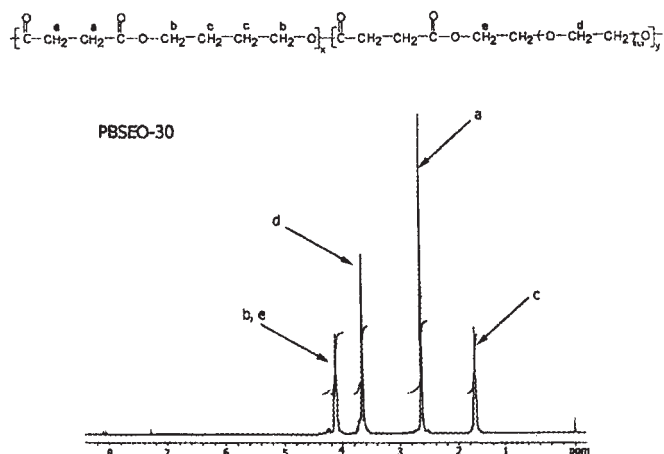


Fig. 1. $^1\text{H-NMR}$ spectrum and structure of the polyester with 30 mass.% of flexible PEOS segments.

The composition of the PTMO series could not be calculated using a peak

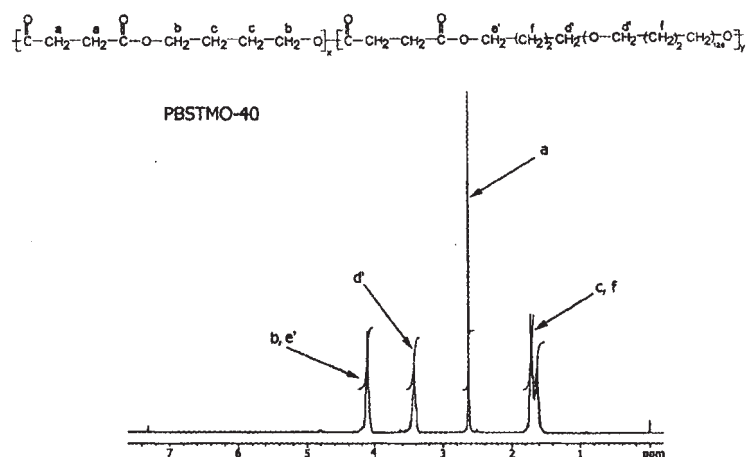


Fig. 2. $^1\text{H-NMR}$ spectrum and structure of the polyester with 40 mass. % of flexible PTMOS segments.

from the butanediol moiety due to the overlapping of the said peak with the signal from similar protons from the PTMO moiety (Fig. 2). In this case the composition could be calculated only by comparing one diol content with total amount of acid moieties. For the PTMO series, the mole fraction of soft PTMOS segments was calculated as the relative intensities of the proton peaks arising from the succinate repeating unit (a) and methylene groups attached to the ether oxygen from the flexible segment (d') using the formula:

$$x(\text{flexible segment}), \text{mol}\% = \frac{I_{d'} / N_{d'}}{I_a / N_a}$$

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 experimentally determined copolyester composition and the theoretical composition calculated from the composition of the feed are given in Table II.

TABLE II. Composition and average length of the hard segment of the synthesized poly(ester-ether)s

Polymer	Mole fraction of flexible segm./mol %		Mass fraction of flexible segm./mass %		L_n
	Theoretical	Experimental	Theoretical	Experimental	
PBSEO-10	1.7	1.3	10.0	7.6	77
PBSEO-20	3.8	3.2	20.0	17.1	31
PBSEO-30	6.4	4.8	30.0	24.3	21
PBSEO-40	9.6	8.1	40.0	35.6	12
PBSEO-50	13.7	12.9	50.0	48.2	8
PBSTMO-10	1.7	1.4	10.0	8.3	71
PBSTMO-20	3.8	3.2	20.0	17.4	31
PBSTMO-30	6.4	4.2	30.0	21.6	24
PBSTMO-40	9.6	6.9	40.0	31.9	15
PBSTMO-50	13.7	12.7	50.0	47.8	8

The obtained results show that in all copolyesters the content of the soft segments was lower than would be expected from the composition of the reaction mixture. However, looking at the mole fractions it can be seen that this difference between the theoretical and experimental composition is in the range of the experimental error of the determination of the composition by $^1\text{H-NMR}$ analysis, which is around 5 %. It may be assumed that the polyether was incorporated to a greater extent in fractions of lower molecular weight, which are more soluble and are probably not precipitated by methanol. The efficiency of the incorporation of the soft segments is between 74 and 94 % for the PEO series and 66 and 93 % for the PTMO series and so there is no significant difference in the efficiency of incorporation of the soft segments between these two series of copolyesters. Also, there is no change in the efficiency of incorporation of soft segments with increasing content of polyether in the feed. It can be concluded that both chosen polyethers have the same reactivity and that they can be efficiently incorporated in the polymer chains. The average sequence length of the hard PBS segments, L_n , was calculated from the mole fraction of PBS as follows:

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

assuming random copolymerization and an average length of the soft segments of 1. These values are also given in Table II. The thermal properties are dependant of the PBS sequence length, and as both series have similar values of L_n (Table II), similar thermal behavior is expected in both series.

Thermal properties of the poly(ester-ether)s

In order to determine the thermal properties of the synthesized polyesters, differential scanning calorimetry was performed whereby two heating runs as well as a cooling run between them were recorded at the same heating/cooling rates. The obtained DSC thermograms are shown in Fig. 3, A and B, for the PEO and PTMO series, respectively.

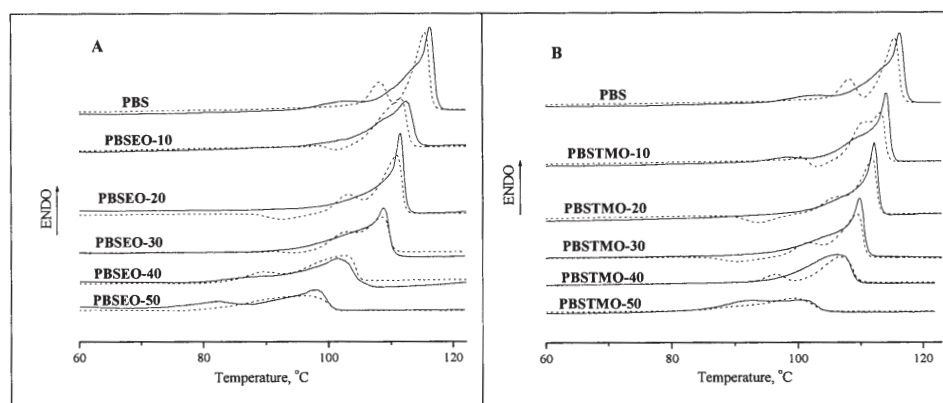


Fig. 3. DSC thermograms of the poly(ester-ether)s with different contents of soft PEOS segments (A) and with different contents of soft PTMOS segments (B): (—) first heating, (---) second heating.

In the DSC thermogram of the first heating run, only one peak in the high temperature region was observed. The melting can be attributed to only the PBS segments (hard phase). There were no melting peaks in the low temperature region, which could be attributed to melting of crystallized polyether segments which could be expected above room temperature. As has been reported, crystallization of soft segments is expected with higher content or length of polyether.^{8,9} With higher soft segments content, the melting peak of the PBS segments broadens (around 24, 33 and 31 °C for PBS, PBSEO-50 and PBSTMO-50, respectively) suggesting a broader crystallite size distribution due to the formation of polymer chains with a distribution of PBS sequence lengths. In the thermograms of the second heating run, the appearance of multiple endothermic peaks is evident in the both series. This behavior can be explained by the melt-recrystallization model²¹ and was observed earlier for PBS and its copolyesters.^{22,23}

From the DSC thermograms of the copolyesters, the melting temperatures and heats of fusion, as well as the crystallization temperatures and enthalpy changes during crystallization were determined. These results are summarized in Table III.

TABLE III. Thermal properties and degree of crystallinity of the poly(ester-ether)s

Polymer	$T_m/^\circ\text{C}$		$\Delta H_m/\text{Jg}^{-1}$		$T_c/^\circ\text{C}$	$\Delta H_c/\text{Jg}^{-1}$	$x_c/\%$	$x_{\text{cPBS}}/\%$
	I run	II run	I run	II run				
PBS	116.3	115.7	89.6	76.2	92.4	80.7	81.1	81.1
PBSEO-10	112.3	111.7	62.7	50.2	77.0	72.5	56.7	61.4
PBSEO-20	111.4	111.0	70.4	59.3	70.6	78.9	63.4	76.9
PBSEO-30	108.7	108.7	70.0	49.8	70.9	63.7	63.3	83.7
PBSEO-40	101.2	102.2	62.2	57.0	54.3	66.8	56.3	87.4
PBSEO-50	97.9	96.4	46.4	38.7	42.9	53.3	42.0	81.8
PBSTMO-10	114.0	113.1	80.2	57.4	81.3	84.1	72.6	79.1
PBSTMO-20	112.1	111.7	71.5	58.4	66.5	79.9	64.7	78.3
PBSTMO-30	109.7	109.5	72.5	59.5	66.5	74.1	65.6	83.7
PBSTMO-40	106.3	106.7	62.9	41.4	76.4	52.5	56.9	83.6
PBSTMO-50	100.1	99.4	47.4	35.7	55.8	52.0	42.9	82.2

The melting temperature of the hard crystalline PBS segments in the poly(ester-ether)s was lower compared to the homopolymer. The melting temperature of the hard segments depends on the average sequence length of the crystallizable units (Table II). Simultaneously, it can be noticed that the melting temperatures of the PTMO copolyesters were slightly higher than those of the copolyesters in the PEO series, as is shown in Fig. 4.

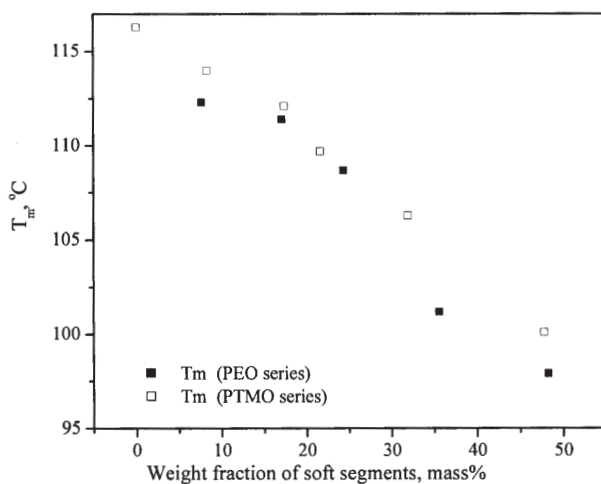


Fig. 4. Melting temperature of the poly(ester-ether)s as a function of composition.

It can be assumed that crystallization of the hard segments is easier when PTMO soft segments are present. The enthalpies of fusion and, thus, the degree of crystallinity of the poly(ester-ether)s are lower than the degree of crystallinity of

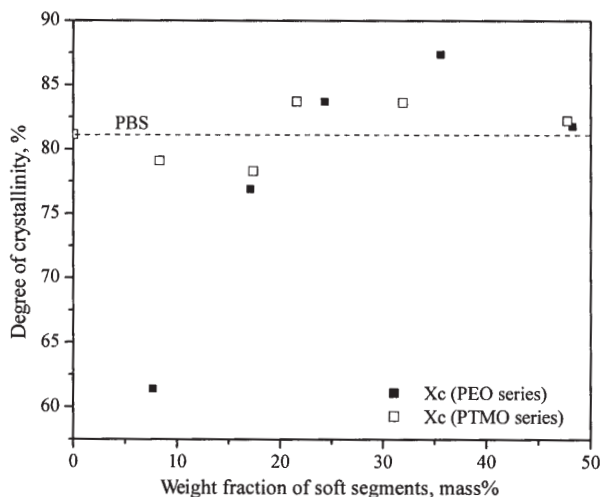


Fig. 5. Normalized degree of crystallinity of the poly(ester-ether)s as a function of copolyester composition.

the homopolymer. The degree of crystallinity of the hard PBS phase is given in Table III. The values are normalized to the PBS content, in order to be able to compare the crystallinity with the PBS homopolymer, using the following formula:

$$x_{c\text{PBS}} = \Delta H_{\text{ml}} / \Delta H^{\circ} w_{\text{PBS}}$$

ΔH_{ml} is the observed heat of fusion of the whole sample, ΔH° is the theoretically calculated heat of fusion of 100 % crystalline PBS (110.5 J/g calculated on the basis of group contribution²⁴) and w_{PBS} is the weight fraction of hard poly(butylene succinate) segments in the sample.

The degree of crystallinity of the whole sample (x_c) was lower than degree of crystallinity of the homopolymer. However, the degree of crystallinity of the hard phase ($x_{c\text{PBS}}$) was similar for all copolymers and close to the degree of crystallinity of PBS. For higher contents of soft segment, the degree of crystallinity of the hard phase (PBS) was even slightly higher than in pure PBS (Fig. 5). The observed extent of enhancement of the degree of crystallinity of PBS was approximately the same for both series, *i.e.*, independent of the type of polyether. This behavior was reported earlier for polyethers of different starting molecular weight.^{8,20} Incorporation of the soft flexible polyether segments probably enhances crystallization.

The degree of undercooling ($\Delta T_h = T_{\text{ml}} - T_c$), an indication of the rate of crystallization was 23.9 °C for PBS and so it can be considered to be a fast crystallizing polyester. The degree of undercooling was increased with incorporation of the soft segments, reaching 55 °C for PBSEO-50 and 64 °C for PBSTMO-50, which means that the rate of crystallization of the poly(ester-ether)s was much lower. This can be another reason for the slightly higher degree of crystallinity of the PBS in the copolyesters, when there is no freezing of the polymer chains and consequentially the hard segments have more time to order in the crystalline structure.

Dynamical mechanical analysis of the poly(ester-ether)s

Dynamical mechanical testing was performed on polymer pellets in the temperature range from 80 °C (in some cases 90 °C) to 160 °C and with varying frequency. For the thermoplastic PBS torsion tests were also performed on a rectangular bar below the melting region. The dependencies of the storage modulus G' on

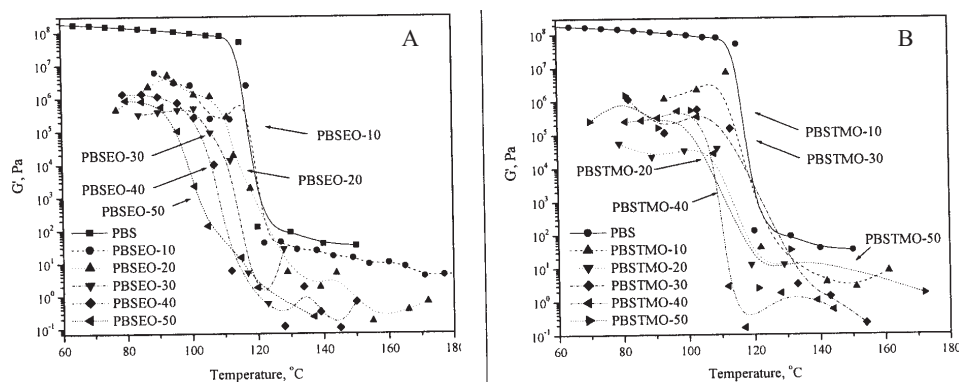


Fig. 6. Storage modulus, G' , dependence on temperature for poly(ester-ether)s with PEO (A) and PTMO (B) in the soft segments at 1 Hz.

temperature for a frequency of 1 Hz are shown in Fig. 6. Both series show similar behavior. A plateau of rubber-like behavior was observed as well as a transition to the molten state. G' for the poly(ester-ether)s in the rubbery plateau was lower than the corresponding value for the homopolymer, PBS, by one to two decades due to the presence of the soft segments and different degree of crystallinity. The transition from the rubbery to the molten state for both the poly(ether-ester)s and PBS was very sharp and is in good agreement with data from the DSC measurements.

From the dynamic mechanical measurements, the complex dynamic viscosity changes with frequency were also recorded (Fig. 7). A similarity between the two

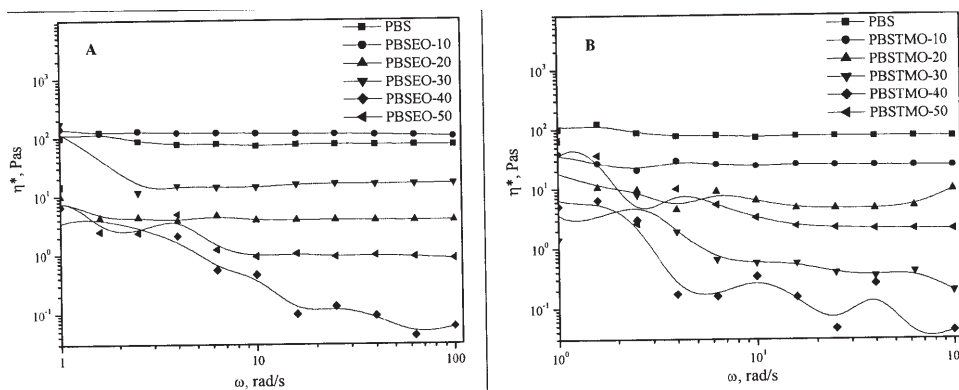


Fig. 7. Complex dynamic viscosity, η^* , versus frequency for the poly(ester-ether)s with PEO (A) and PTMO (B) in the soft segments at 130 °C.

series is also observed in these dependencies. The poly(ester-ether)s of both series show Newtonian behavior in the melt, *i.e.*, there was no change in η^* with change of frequency. The scattering observed for PBSEO-50 and PBSTMO-50 can be a consequence of the low values of η^* that were on the limit of the sensitivity of the instrument used.

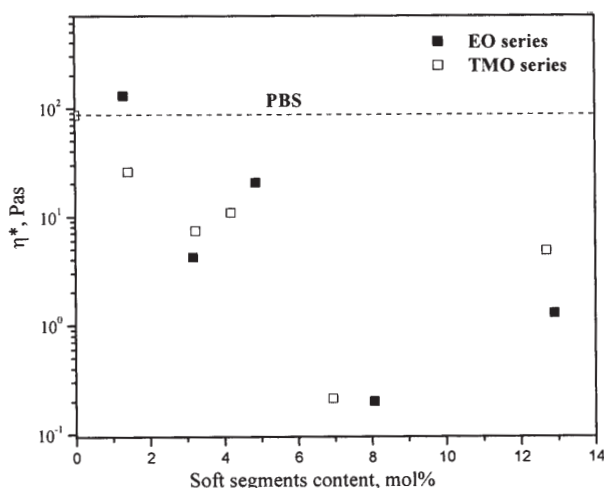


Fig. 8. Dependence of the complex dynamic viscosity, η^* (1 Hz, 130 °C), on the poly(ester-ether) composition.

The change in the complex dynamic viscosity with composition of the poly(ether-ester)s is shown in Fig. 8. It is evident that with increasing soft segment content, the viscosity was lower as a consequence of the increased mobility of the polymer chains. In some cases there is disagreement from the observed trend (PBSEO-10, PBSEO-30, PBSEO-50 and PBSTMO-50) which can be explained by the different molecular weights of the poly(ester-ether)s which also have an influence on the value of η^* but in the opposite direction.

Enzymatic degradation

The biodegradability of the poly(ester-ether)s was investigated by monitoring the weight loss of polymer films exposed to an enzyme in phosphate buffer solution with time. As was previously mentioned, only the poly(ester-ether)s with $[\eta]$ above 60 cm³/g gave good films, so the enzymatic degradation tests were carried out only for PBS and the poly(ester-ether)s with 10 mass % of soft segments. The time changes of the weight losses of the polymer films divided by the total surface area are shown in Fig. 9.

The results obtained in the blank tests (without addition of the enzyme and carried out for 150 h) are also shown in Fig. 9. As can be seen from Fig. 9, the weight losses for the poly(ester-ether)s are higher than those obtained in the tests performed with PBS. This increase can be explained by the increased hydrophilicity of the copolymers, as well as by the decrease in the crystallinity of poly(es-

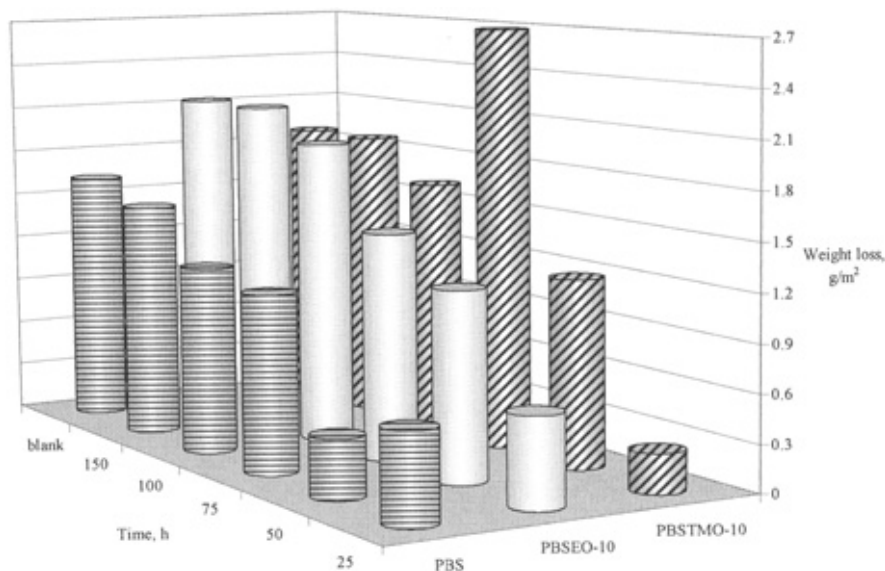


Fig. 9. Normalized weight losses of the polymer samples in the enzymatic degradation tests with *Candida cylindracea* lipase.

ter-ether)s. Introduction of polyether soft segments is good way to tailor the biodegradability properties of aliphatic polyesters. The obtained results suggest that poly(ester-ether)s with PEO in the soft segments are more susceptible to hydrolysis than those based on PTMO, which is to be expected from the lower hydrophilicity of PTMO compared with PEO.⁸ However, this difference is not so pronounced and future tests on poly(ether-ester)s with higher contents of hydrophilic segments will reveal the true difference between these two types of soft segments. The weight losses obtained in the blank tests were of the same order of magnitude as the ones obtained in the presence of the enzyme. In Fig. 9, only the weight losses after 150 h of incubation for the blank test are shown. The chosen lipase at this concentration does not have any catalytic effect on the hydrolysis of polyesters of this type.

CONCLUSION

By applying a transesterification reaction in the bulk, the successful synthesis of two series of poly(ester-ether)s was achieved. On the basis of ¹H-NMR spectroscopy, the compositions of the poly(ester-ether)s were shown to be close to the composition of the feed. Also no difference in the reactivity of the two employed polyethers was noticed. The melting temperatures of the poly(ester-ether)s were lower than that of the homopolymer. The degree of crystallinity of the poly(ester-ether)s was also lower than that of PBS, but the degrees of crystallinity of the hard phase were close to that of PBS or even slightly higher due to the presence of flexible segments that enhance crystallization. The thermal properties of the po-

ly(ester-ether)s at this content of soft segments were not influenced very much by the type of polyether used. Dynamic mechanical measurements showed that the storage modulus of the poly(ester-ether)s were lower than the corresponding value for PBS, and that Newtonian behavior of the melt was observed with all the synthesized polyesters. The increased flexibility of the polymer chains has a pronounced influence on the complex dynamic viscosity with increasing content of soft segments. The results obtained in the biodegradation tests showed that the introduction of the hydrophilic polyether segments increased the biodegradability and is good way to tailor the biodegradability properties of aliphatic polyesters. Also, the difference in the hydrophilicity of two types of employed polyethers results in two series of poly(ester-ether)s having different biodegradation properties.

ИЗВОД

СИНТЕЗА И КАРАТЕРИЗАЦИЈА БИОДЕГРАДАБЛНИХ АЛИФАТИЧНИХ
КОПОЛИЕСТАРА МОДИФИКОВАНИХ МЕКИМ ХИДРОФИЛНИМ
СЕКМЕНТИМА

ДАНИЈЕЛА ЈОВАНОВИЋ, МАРИЈА С. НИКОЛИЋ и ЈАСНА ЂОНЛАГИЋ

Технолошко-мешалурски факултет Универзитета у Београду, Карнегијева 4, 11000 Београд

У оквиру овог рада испитана је синтеза и физичка својства две серије сегментираних поли(естар-етара) на бази поли(бутилен-сукцината) и два типа различитих полиетара. Поли(естар-етри) су синтетисани реакцијом трансестерификације полазећи од диметил-сукцината, 1,4-бутандиола и поли(етилен-оксида) (РЕО, $M_n = 1000$ g/mol) у првој серији, и поли(тетраметилен-оксида) (РТМО, $M_n = 1000$ g/mol) у другој серији. Масени удео меких сегмената у обе серије је вариран од 10 до 50 мас. %. Изучаван је утицај увођења различитих полиетарских меких сегмената на структуру, као и термичка и реолошка својства. На основу састава поли(естар-етара) одређених из $^1\text{H-NMR}$ спектра је показано да је увођење меких полиетарских сегмената успешно изведено реакцијом трансестерификације у растопу. Моларна маса је процењена на основу граничних вискозитетних бројева и комплексних динамичких вискозитета. Диференцијалном скенирајућом калориметријом је утврђено да се увођењем меких сегмената снижавају температуре топљења и кристализације тврде фазе. Степен кристаличности целог узорка, процењен на основу промена енталпија топљења, смањује се, док је степен кристаличности тврде фазе исти као код хомополимера или нешто већи при већим уделима меких сегмената. Испитивање утицаја састава на реолошка својства поли(естар-етара) је изведено динамичко-механичком анализом. Резултати добијени у тестовима ензимске разградње показују да се биодеграбилност повећава са повећањем хидрофилности полимера.

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