

Synthesis and Characterization of Copolymers Based on Poly(butylene terephthalate) and Ethylene Oxide-Poly(dimethylsiloxane)-Ethylene Oxide

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ABSTRACT: A series of thermoplastic elastomers based on ethylene oxide-poly(dimethylsiloxane)-ethylene oxide (EO-PDMS-EO), as the soft segment, and poly(butylene terephthalate) (PBT), as the hard segment, were synthesized by catalyzed two-step, melt transesterification reaction of dimethyl terephthalate (DMT) with 1,4-butanediol (BD) and α,ω -dihydroxy-(EO-PDMS-EO). Copolymers with a content of hard PBT segments between 40 and 90 mass % and a constant length of the soft EO-PDMS-EO segments were prepared. The siloxane prepolymer with hydrophilic terminal EO units was used to improve the miscibility between the polar comonomers, DMT and BD, and the nonpolar PDMS. The molecular structure and composition of the copolymers were determined by ¹H-NMR spectroscopy, whereas the effectiveness of the incorporation of α,ω -dihydroxy-(EO-PDMS-EO) into the copoly-

mer chains was verified by chloroform extraction. The effects of the structure and composition of the copolymers on the melting temperatures and the degree of crystallinity, as well as on the thermal degradation stability and some rheological properties, were studied. It was demonstrated that the degree of crystallinity, the melting and crystallization temperatures of the copolymers increased with increasing mass fraction of the PBT segments. The thermal stability of the copolymers was lower than that of PBT homopolymer, because of the presence of thermolabile ether bonds in the soft segments. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3205–3216, 2010

Key words: thermoplastics; elastomers; poly(ester-ether-siloxane)s; α,ω -dihydroxy-[ethylene oxide-poly(dimethylsiloxane)-ethylene oxide]; thermal properties

INTRODUCTION

Thermoplastic elastomers have found wide applications in many industrial branches because of their excellent mechanical and physical properties. These polymers combine the mechanical properties of chemically crosslinked elastomers and the easiness of processability of thermoplastic materials.^{1,2}

Block copolymers belonging to the class of thermoplastic elastomers, which have soft segments based on poly(siloxane)s, show lower glass transition temperatures, higher thermal and thermo-oxidative stability, higher resistance to UV-radiation, atomic oxygen, and ozone, as well as enhanced permeability to many gases, hydrophobicity, biocompatibility, and resistance to many solvents in comparison with common organic polymers. Hard, glassy, or crystalline segments in such copolymers, which provide physical crosslinking, can be different organic poly-

mers, such as aromatic esters, urethanes, amides, and sulfones. Reactive, telechelic siloxane oligomers (α,ω -telechelic siloxanes) are the most important starting material for the synthesis of siloxane-containing copolymers with properties of thermoplastic elastomers.^{3,4}

In most of the published reports concerning siloxane-containing copolymers, the soft segment was almost exclusively poly(dimethylsiloxane). The nonpolar nature of the PDMS together with very low levels of intermolecular attractions leads to the formation of thermodynamically incompatible blends with almost all other polymers. This is reflected in the very low value of the solubility parameters of PDMS [$\delta = 15 \text{ (J cm}^{-3}\text{)}^{1/2}$]^{4,5} when compared with other polymers [$\delta = 15.4\text{--}28.0 \text{ (J cm}^{-3}\text{)}^{1/2}$].⁶ This is a very important driving force in the formation of two-phase microstructure in PDMS-containing copolymers. Another very important factor that makes the morphology of siloxane copolymers somewhat unusual is the fact that at room temperature (20–25°C), PDMS is about 150°C above its glass transition temperature. At these temperatures, because of the absence of inter- and intramolecular interactions, the PDMS segments behave like a nonpolar viscous liquid, thus providing perfect

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conditions for the formation of phase-separated copolymer structures. In many cases, a siloxane molar mass as low as 500–600 g mol⁻¹ (6–8 siloxane repeat units) and an organic segment having only a single repeat unit is sufficient to obtain two-phase morphologies.⁴ Because of the two-phase microstructure, the copolymers possess excellent mechanical properties of chemically crosslinked elastomers, that is, such a material is self-reinforced. At elevated temperatures, the physical crosslinking disappears, allowing the copolymer to soften and flow like a thermoplastic material and enabling it to be processed in the melt by techniques such as injection molding.^{1,2}

Several studies on multiblock copolymers based on poly(butylene terephthalate), PBT, hard segments and soft segments based only on poly(organosiloxane)s or on combinations of poly(siloxane)s and polyethers have been presented since 1990.^{7–20} The incorporation of poly(organosiloxane) segments into a polyester backbone results in improved clarity, surface smoothness, and nonsticking properties, as well as good film, fiber, and hydrophobic properties of the resulting copolymers, which is described in the patent literature.^{21–26}

Our research in the field of siloxane-containing copolymers is related to the synthesis of thermoplastic poly(ester-siloxane)s (TPES) and poly(ester-ether-siloxane)s, (TPEES), based on PBT as the hard segment, and different siloxane prepolymers as the soft segments. The TPES and TPEES were synthesized by catalyzed two-step transesterification, from dimethyl terephthalate (DMT), 1,4-butanediol (BD), and different siloxane prepolymers. The poly(ester-siloxane)s based on dicarboxypropyl-(PDMS-CP)-terminated poly(dimethylsiloxane) were inhomogeneous.^{15–17,19} All the prepared samples were partially soluble in chloroform, as a consequence of their significant structural and compositional inhomogeneity. Siloxane triblock prepolymer with poly(propylene oxide) (PPO) terminal blocks [α,ω -dihydroxy-(PPO-PDMS-PPO)] was used in further investigations to increase the miscibility of the polar and nonpolar reactants during copolymer synthesis.^{18,19} However, the presence of ether PPO chains in the siloxane-containing prepolymer did not improve the homogeneity of the prepared TPEES samples. All the TPEES samples were partially soluble in chloroform, as were the TPES samples based on PDMS-CP prepolymer. In the case of the PPO-PDMS-PPO TPEES, it was concluded that the compatibilizing effect between PBT and PDMS was not realized.

In this study, a series of TPEES was prepared from DMT, BD, and α,ω -dihydroxy-ethylene oxide-poly(dimethylsiloxane)-ethylene oxide (α,ω -dihydroxy-EO-PDMS-EO). The prepolymer consisted of the central PDMS-block and hydrophilic EO terminal

units, which served as a compatibilizer between the nonpolar PDMS and the polar comonomers (DMT and BD). The mass ratio between the hard and soft segments was in the range from 40 : 60 to 90 : 10. Simultaneously, the length of the hard segments was increased with increasing mass ratio of hard to soft segments, whereas the length of the soft segments remained constant. The results on the synthesis and characterization of these TPEES, differing in composition and structure of the molecular chains, are presented in this article.

EXPERIMENTAL PART

Reagents

α,ω -Dihydroxy-(EO-PDMS-EO) (from ABCR, $\overline{M}_n = 1000$ g mol⁻¹) was dried over molecular sieves (0.4 nm) before use. The number-average molar mass (\overline{M}_n) of the α,ω -dihydroxy-(EO-PDMS-EO), determined by ¹H-NMR spectroscopy, was 1200 g mol⁻¹, and this value was used in the calculations of the composition of reaction mixtures for the synthesis of the poly(ester-ether-siloxane)s. The molar mass of the central PDMS-block was $\overline{M}_{\text{PDMS}} = 1090$ g mol⁻¹, whereas the terminal ethylene oxide sequences consisted of one unit. Dimethyl terephthalate (from Merck) was purified by recrystallization from absolute ethanol and dried at 80°C for 24 h before use. 1,4-Butanediol (from Aldrich) was distilled and dried over molecular sieves before use. Tetra-*n*-butyl-titanate (Ti(OBu)₄) (from Aldrich) was used as a solution in dry *n*-butanol (1 : 9 vol). *N,N'*-Diphenyl-*p*-phenylenediamine (DPPD) (from Bayer) was used as received.

Poly(ester-ether-siloxane) synthesis

The TPEESs were synthesized by a catalyzed two-step reaction involving transesterification and polycondensation in the melt.^{15–19} The reactants were DMT, BD, and α,ω -dihydroxy-(EO-PDMS-EO). The amounts of the individual reactants were fixed to obtain the desired mass ratio of hard to soft segments in the copolymer products (in the range from 90 : 10 to 40 : 60), whereas the ratio of the reacting –OH groups (from BD and α,ω -dihydroxy-(EO-PDMS-EO)) and the –COOCH₃ groups (from DMT) was 3 : 2. The catalyst was tetra-*n*-butyl-titanate (2.0 mmol Ti(OBu)₄/1 mol DMT) and the antioxidant was DPPD (0.5 mass % in the starting reaction mixture).^{18,27} It was found that the catalyst should be added in two portions: 60 mass % at the beginning of the reaction and the remaining 40 mass %, before commencement of the second step of the reaction.¹⁵

All the syntheses were performed in a Pyrex glass laboratory reactor equipped with a magnetic stirrer,

thermometer, nitrogen gas inlet, and a distillation condenser. The reactor was placed in a silicone oil bath. The starting reaction mixture, for example, for TPEES-50, 17.8 g (0.092 mol) DMT, 11.6 g (0.128 mol) BD, 15.3 g (0.014 mol) α,ω -dihydroxy-(EO-PDMS-EO), and 0.04 g (0.110 mmol) of catalyst, was charged into the reactor at room temperature and then heated under nitrogen at atmospheric pressure for 2.5–3.0 h. The first step, transesterification, was carried out from 160 to 220°C, when the methanol was distilled off. After the first step, DPPD stabilizer (0.224 g) and the second portion of catalyst (0.023 g, 0.074 mmol) were added and vacuum was applied. The reaction mixture was kept at 245°C, under vacuum ($P < 67$ Pa) for 4.5 h. Finally, after 4.5 h of polycondensation, the obtained viscous slurry was allowed to cool down to room temperature in the reactor under nitrogen.

During the synthesis, TPEES-40-pt (40 mass % of soft segments), the polycondensation was performed for 6.0 h, under the same conditions as described previously. After 1.5, 3.0, and 4.5 h, a small part of the reaction mixture was removed from the reactor, for measurements of the inherent viscosity. After 6.0 h of polycondensation, the obtained viscous slurry was cooled down to room temperature in the reactor under nitrogen.

Soxlet extraction of the TPEES samples

The synthesized TPEES samples, weight about 0.15 g, were extracted with 150 cm³ of chloroform in a Soxlet apparatus for 24 h. The extracted and insoluble fractions were dried for 5 h at 105°C. The weights of the dry soluble and insoluble fractions were measured, and the samples were analyzed by ¹H-NMR spectroscopy to determine their structure and composition, as well as the average length of the segments in each fraction.

Measurements

¹H-NMR (200 MHz) spectra were obtained on a Varian Gemini-200 instrument. The TPEESs were measured as solutions in CF₃COOD. The solvent was simultaneously used as the internal standard.

The inherent viscosities, η_{inh} , of the TPEESs were measured in a mixture of phenol/trichloroethylene/toluene (1 : 1 : 2 vol) at 30°C, using an Ubbelohde viscometer. The concentration of the copolymer in solution was 0.5 g dL⁻¹.

Differential scanning calorimetry (DSC) was performed using a TA Instruments SDT Q600 thermal analyzer. The DSC scans were recorded under a dynamic nitrogen atmosphere (flow rate 100 cm³ min⁻¹) at a heating and cooling rate of 10°C min⁻¹ (two scans were run for each sample). The weight of

the samples was ~ 10 mg. The samples were analyzed between 50 and 250°C for the determination of the melting point (T_m) and the crystallization point (T_c) of the hard segment.

Wide angle X-ray scattering (WAXS) was performed using a PW1710 diffractometer with a Cu-K α radiation using copper anode (tube: 40 kV, 30 mA, $\lambda = 0.154178$ nm). From the WAXS data, the percent of crystallinity was calculated by peak deconvolution and subsequent determination of the relative areas under the amorphous halo and the crystalline peaks of the X-ray diffraction scan. The ratio of the area under the crystalline peaks to the total (amorphous + crystalline) area gave the degree of crystallinity.

Thermal gravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 in nitrogen and oxygen, in the temperature interval from 30 to 700°C. The gas flow rate was 100 cm³ min⁻¹, and the heating rate was 10°C min⁻¹ in all cases. The average weights of the samples were around 10 mg.

Dynamic mechanical analysis was performed using a Rheometrics mechanical spectrometer RMS-605. The complex dynamic viscosities, η^* , of the TPEESs melts were recorded operating in the dynamic shear mode between two parallel plates, at 235°C. The frequency was varied from 0.1 to 100 rad s⁻¹. The radius of the samples was 25 mm and the thickness was about 1.0 mm. The dynamic mechanical analysis of the TPEESs was also performed under torsion rectangular conditions on molded polymers bars (63.0 mm \times 12.4 mm \times 1.0 mm) in the temperature range from 25 to 170°C.

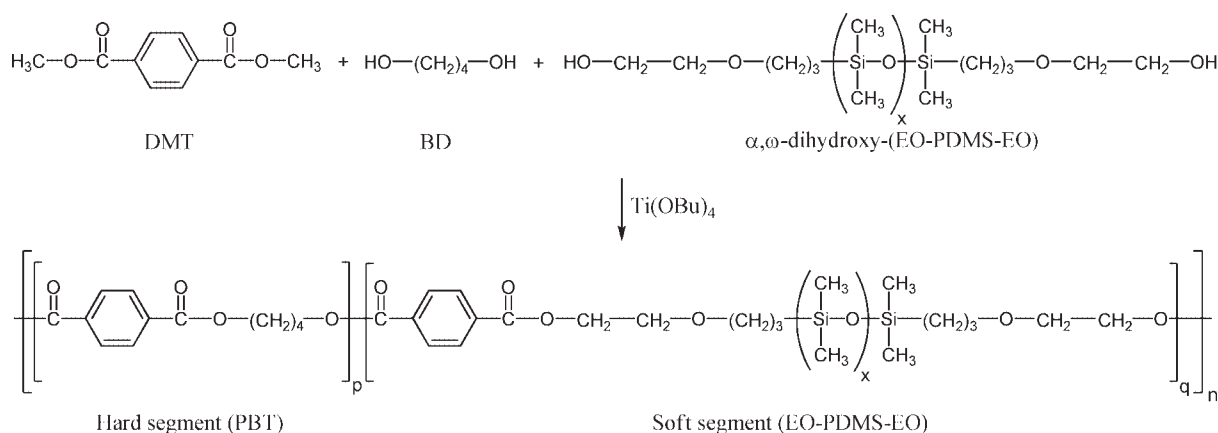
RESULTS AND DISCUSSION

The synthesis of the TPEES copolymers is shown in Scheme 1.

The transesterification of dimethylterephthalate with BD and α,ω -dihydroxy-(EO-PDMS-EO) was carried out in the temperature range 160–220°C at normal pressure in the presence of Ti(OBu)₄ as catalyst, when oligomeric esters were formed. The polycondensation was performed by heating the mixture to 245°C under reduced pressure to remove the excess BD and hence produce chain extension. DPPD, a heat stabilizer, was used to protect the polymer chains from thermal degradation during the polycondensation reaction at 245°C.

Determination of the optimal reaction time

The influence of the time of polycondensation on the inherent viscosity, that is, on the molar mass, of the copolymer was investigated during the synthesis of TPEES-40-pt. Samples of the reaction mixtures were removed during the polycondensation reaction, and their inherent viscosity (η_{inh}) was measured in a



Scheme 1 Synthesis of the thermoplastic poly(ester-ether-siloxane)s.

mixture phenol/trichloroethylene/toluene. As poly(ester-ether-siloxane)s are not soluble in common organic solvents, such as tetrahydrofuran or chloroform, which are usually used for GPC,^{14,18} the η_{inh} was used as an indicator of the molar mass. The inherent viscosity was measured after 1.5, 3.0, 4.5, and 6.0 h. From these results, it was concluded that the optimal time for performing polycondensation under the described experimental conditions was 4.5 h. The inherent viscosity of TPEES-40-pt during the course of polycondensation first increased with increasing polycondensation time, reached a maximum, and finally decreased slowly ($\eta_{\text{inh}} = 0.43 \text{ dL g}^{-1}$ for 1.5 h, 0.64 for 3.0 h, 0.70 for 4.5 h, and 0.68 for 6.0 h). Such behavior was probably the consequence of the occurrence of thermal degradation reactions during longer polycondensation time at 245°C. Thus, a polycondensation time of 4.5 h under a pressure lower than 67 Pa was used for all the other syntheses of TPEESs.

Series of TPEESs with different structure and composition

A series of TPEES was synthesized with the determined optimal polycondensation time of 4.5 h. The molar ratio of the starting reactants was selected to result in copolymers with a hard to soft segment mass ratio from 90 : 10 to 40 : 60, whereas the molar mass of the soft segment was constant. In this manner, six TPEES samples with different hard segment lengths were obtained. The average degree of polymerization of the hard PBT segment, that is, the number of butylenes terephthalate units in the PBT segments (p in Scheme 1), increased with increasing mass fraction of PBT segment in the copolymer. The fractions of PBT segments in TPEES and the average degrees of polymerization of PBT as well as the in-

herent viscosities and complex dynamic viscosities (η^*) at 235°C are given in Table I. The Mark-Houwink constants are not known for these poly(ester-ether-siloxane)s, which relate the intrinsic viscosity $[\eta]$ to the molecular weight M_v and depend on the polymer composition, the solvent, and temperature. Therefore, values of inherent viscosity (η_{inh}) are used for comparison of the copolymers under this study.

The inherent viscosities increased from 0.38 to 0.76 dL g^{-1} with increasing mass fraction of EO-PDMS-EO segments from 10 to 50 mass %. The highest value was obtained for the sample TPEES-50, with a mass ratio of hard and soft segments of 50 : 50. With further increasing of the mass fraction of soft segments to 60%, η_{inh} decreased to 0.47 dL g^{-1} .

The complex dynamic viscosity shows the maximums when the mass fractions of EO-PDMS-EO were 40 and 50% (913 and 864 Pa s, respectively), whereas all the other samples had much lower values of η^* , between 6 and 32 Pa s (Table I). This indicates that the molar masses of the samples TPEES-40 and TPEES-50 were probably above the critical values for poly(ester-ether-siloxane)s. The agreement between η^* and η_{inh} was quite good, so the samples with the highest values of η^* had the highest values of η_{inh} . The recorded changes of η^* with frequency at 235°C are presented in Figure 1. From the complex dynamic viscosity measurements, it can be concluded that the synthesized TPEES exhibit pseudo-plastic behavior over a wide temperature range.

Structure and composition of the synthesized TPEESs

The molecular structure of the poly(ester-ether-siloxane)s was investigated by ¹H-NMR spectroscopy. Two ¹H-NMR spectra of TPEES-40 and TPEES-60

TABLE I
Chemical Composition, Inherent (η_{inh}), and Complex Dynamic (η^*) Viscosity of the Poly(ester-ether-siloxane)s

Sample	Fraction of PBT segments		Molar ratio PBT/ EO-PDMS-EO		η_{inh} , dL g ⁻¹	η^* (235°C and 6.31 rad s ⁻¹), Pa s
	Mass % ^a	Mass % (NMR)	p^a	p (NMR)		
TPEES-10	90	93.4	50.3	82.3	0.38	32
TPEES-20	80	83.9	22.4	31.3	0.38	12
TPEES-30	70	73.9	13.1	17.2	0.43	14
TPEES-40	60	63.6	8.4	10.6	0.61	913
TPEES-50	50	53.4	5.6	6.9	0.76	864
TPEES-60	40	43.9	3.7	4.7	0.47	6

^a $p = \frac{\text{molPBT}}{1 \text{ mol(EO-PDMS-EO)}}$; predetermined by the reaction mixture compositions.

are presented in Figure 2 to have a better insight in composition difference of the poly(ester-ether-siloxane)s. The ¹H-NMR spectrum shows chemical shifts at $\delta = 0.28$ – 0.53 ppm of the Si–CH₃ protons; at 1.03, 1.92, and 3.94 ppm of the CH₂ protons from the PDMS propyl groups; at 4.22 and 4.79 ppm of the methylene protons from ethylene oxide; at 8.20 ppm of the aromatic protons, at 2.19 and 4.67 ppm, respectively, of the central and terminal methylene protons of the BD residue.

Dissolution of TPEES in CF₃COOD is followed by the siloxane-equilibration reaction within the siloxane block and by the production of cyclosiloxanes. As a consequence, the signal of the Si–CH₃ protons splits, but the quantity of Si–CH₃ protons remains the same before and after equilibration in the PDMS segments and, therefore, has no influence on the calculations from ¹H-NMR spectra.^{15–18}

The molar and mass fractions of hard and soft segments, as well as the average degree of polymerization of the PBT segments (p), were calculated from the ratio of the integrals of the central –CH₂– protons of the BD residue [$I(\text{CH}_2)$] and of the Si–CH₃ protons [$I(\text{SiCH}_3)$]:

$$x_{HS} = \frac{I(\text{CH}_2)}{I(\text{CH}_2) + \frac{I(\text{SiCH}_3)}{6 \cdot \bar{X}_x + 6}}; \quad x_{SS} = 1 - x_{HS}$$

$$w_{HS} = \frac{x_{HS} \cdot M_{HS}}{x_{HS} \cdot M_{HS} + x_{SS} \cdot M_{SS}}; \quad w_{SS} = 1 - w_{HS}$$

and

$$p_{(\text{PBT})} = \frac{x_{TS}}{x_{MS}},$$

where x_{HS} and x_{SS} are the mole fractions of hard and soft segments, respectively, whereas w_{HS} and w_{SS} are the mass fractions of hard and soft segments, respectively, $M_{HS} = 220$ g mol⁻¹ is the molar mass of butylene terephthalate unit, $M_{SS} = 1330$ g mol⁻¹ is

the molar mass of the EO-PDMS-EO segment, and $\bar{X}_x = 12.8$ (the degree of polymerization of the PDMS-block in the prepolymer). The degree of polymerization of the PDMS-block in the prepolymer was calculated from ¹H-NMR spectrum of prepolymer in the following way:

$$\frac{I(\text{SiCH}_3)}{I(\text{CH}_2)} = \frac{6 \cdot \bar{X}_x + 6}{4}$$

$$\bar{X}_x = \left[\frac{2 \cdot I(\text{SiCH}_3)}{3 \cdot I(\text{CH}_2)} - 1 \right]$$

$$\bar{X}_x = 12.80,$$

where [$I(\text{SiCH}_3)$] is the relative intensity of the Si–CH₃ protons, whereas [$I(\text{CH}_2)$] is the relative intensity of the terminal –CH₂– protons in the ethylene oxide residue.

The data obtained from the ¹H-NMR spectra are presented in Table I. The obtained values for the mass fractions of the PBT segments were 43.9–93.4%, which agrees well with the values that were predetermined from the reaction mixture compositions

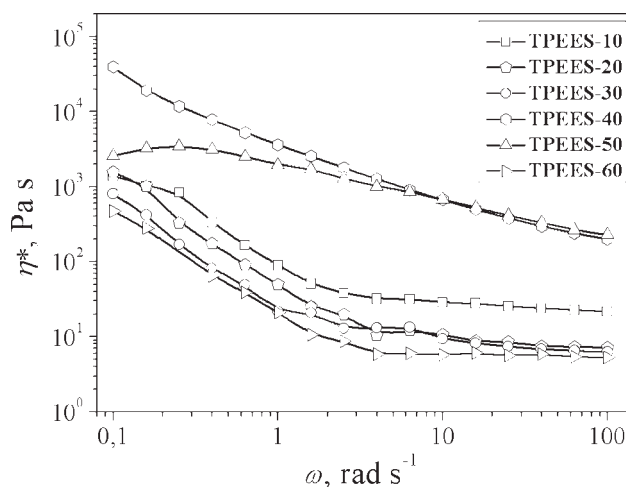


Figure 1 Complex dynamic viscosity versus frequency at 235°C for the TPEES.

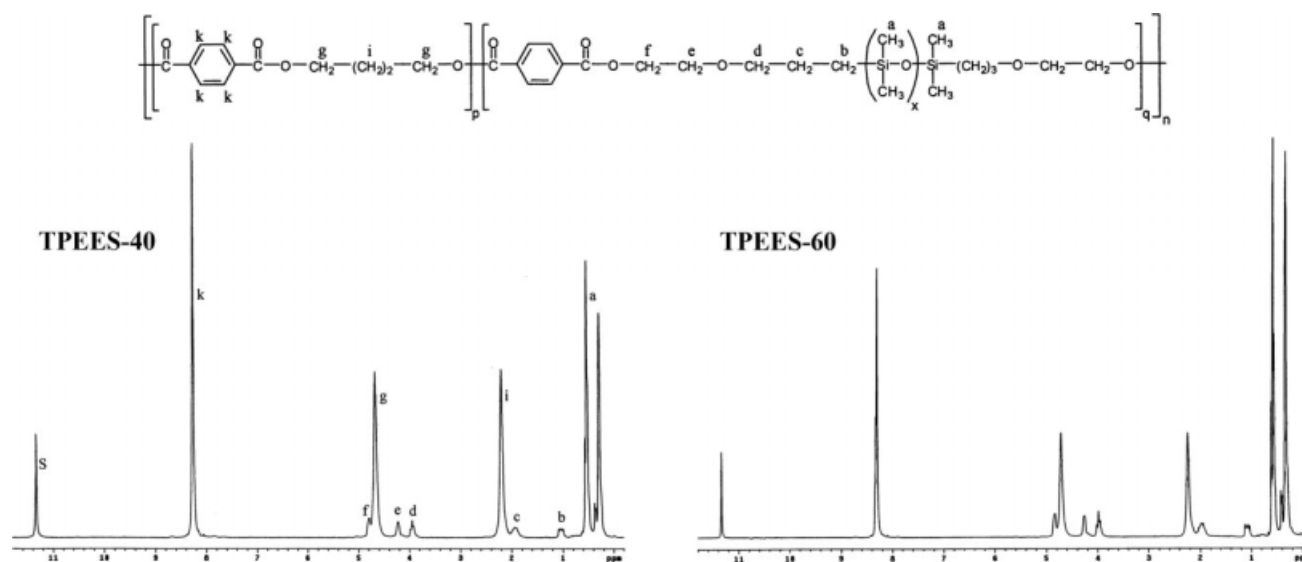


Figure 2 $^1\text{H-NMR}$ spectra for the TPEES-40 and TPEES-60 samples.

(presented in Table I). The average length (degree of polymerization) of the PBT segments was calculated according to 1 mol of soft PDMS segment ($q = 1$ in Scheme 1). The possibility of $q > 1$ was small, because of the relatively low molar fraction of the α,ω -dihydroxy-EO-PDMS-EO prepolymer in the starting reaction mixtures (1.2–18.4 mol %). The average length of the hard segments decreased from 82.3 (TPEES-10) to 4.7 (TPEES-60), as a consequence of the decrease of their mass fractions.

The effectiveness of the incorporation of EO-PDMS-EO segments into the copolymer chains was proven by Soxhlet extraction with chloroform. It is well known that PBT homopolymer is insoluble in chloroform, whereas the α,ω -dihydroxy-EO-PDMS-EO prepolymer is soluble and therefore extractable with chloroform. The solubility of the copolymers depends on the content of PBT, that is, they are generally insoluble but those with a very low content of PBT are soluble.^{15–19} The obtained results showed that all the TPEES samples were comprised from a soluble and insoluble fraction (Table II). Examination by $^1\text{H-NMR}$ spectroscopy showed that soluble and insoluble fraction differed in both their composition

and structure, containing considerably different amounts of EO-PDMS-EO and PBT segments. The TPEES samples lost 3.3–55.9% of their mass during extraction with chloroform, the highest value of extracted fraction corresponding to the sample TPEES-60, with the highest content of soft segments in the copolymer. The soluble fraction contained 81.9–85.4 mass % of EO-PDMS-EO segments, whereas the insoluble fraction contained 3.9–23.2 mass % of EO-PDMS-EO segments. The mass fraction of soft segments in the soluble fraction increased with increasing mass fraction of soft segments in the copolymer. The calculated value of p (Scheme 1) in the soluble fraction was very small ($p_{\text{sol}} = 1.0\text{--}1.3$), whereas in the insoluble fraction it was higher ($p_{\text{ins}} = 20.0\text{--}148.3$) and again increased with increasing mass fraction of PBT segments.

Thus, all samples were still inhomogeneous in terms of composition and structure in spite of the use of EO-PDMS-EO as the prepolymer with terminal ethylene oxide units. However, both the extracted and insoluble fractions still had a multi-block structure, with very short PBT segments in the soluble fractions and very long PBT segments in the

TABLE II
 $^1\text{H-NMR}$ Analysis of the Chloroform-Soluble and Insoluble Parts of the TPEESs

Sample	Soluble part			Insoluble part		
	Fraction, mass %	Mass ratio PBT EO-PDMS-EO	p_{sol}	Fraction, mass %	Mass ratio PBT EO-PDMS-EO	p_{ins}
TPEES-10	3.3	17.6/82.4	1.3	96.7	96.1/3.9	148.3
TPEES-20	12.8	17.5/82.5	1.3	87.2	93.3/6.7	84.5
TPEES-30	25.5	17.7/82.3	1.3	74.5	90.4/9.6	56.8
TPEES-40	26.1	14.6/85.4	1.0	73.9	84.6/15.4	33.5
TPEES-50	33.6	16.9/83.1	1.2	66.4	76.8/23.2	20.0
TPEES-60	55.9	18.1/81.9	1.3	44.1	81.5/18.5	26.8

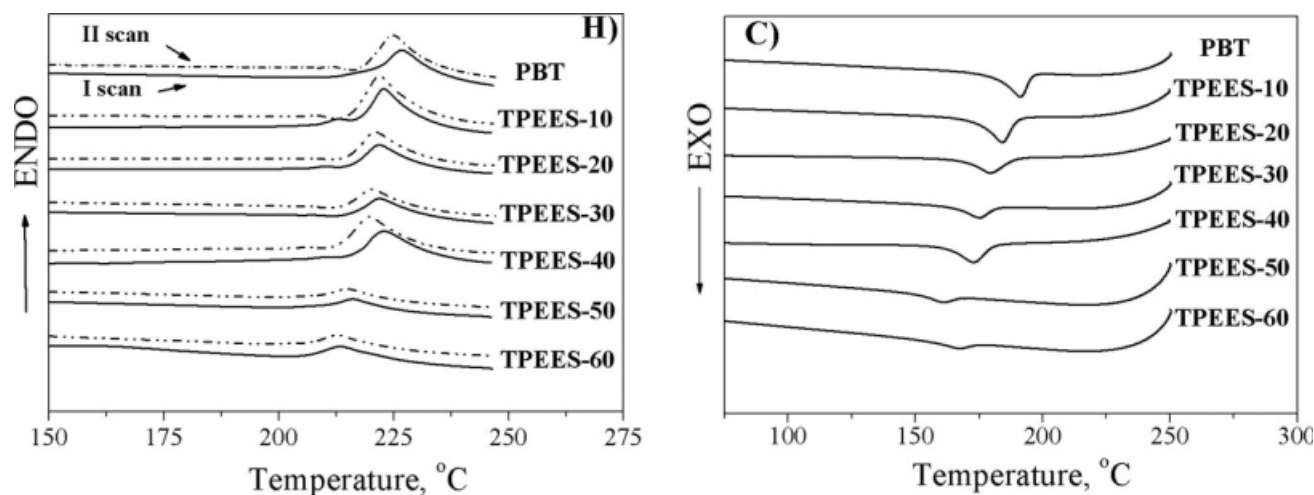


Figure 3 DSC curves of TPEES obtained during: (H) heating and (C) cooling.

insoluble fractions. It can be concluded that the presence of short ethylene oxide blocks (only one repeating unit) in prepolymer was not sufficient to improve the miscibility between the nonpolar PDMS and the polar comonomers, DMT and BD, in spite of its high-solubility parameter [$\delta_{\text{PEO}} = 20.2 \text{ (J cm}^{-3})^{1/2}$],⁵ which is close to the solubility parameter of PBT [$\delta_{\text{PBT}} = 23.0 \text{ (J cm}^{-3})^{1/2}$].⁶ To achieve better miscibility, a prepolymer with longer EO sequences could be a better choice.

DSC analysis of the poly(ester-ether-siloxane)s

The synthesized poly(ester-ether-siloxane)s are semi-crystalline polymers. The melting and crystallization temperatures of the hard segments were observed by DSC analysis.

The DSC measurements were performed using the so-called triple cycle, "heating-cooling-heating," to determine the melting temperature (T_m), the enthalpy of melting (ΔH_m), the crystallization temperature (T_c), the enthalpy of crystallization (ΔH_c), and the degree of crystallinity of the TPEES samples and, for the sake of comparison, of the PBT homopolymer, synthesized in a similar way.¹⁶ The results are presented in Figure 3 and Table III.

The DSC curves show different high-temperature transitions corresponding to the melting and crystallization temperature of the PBT segments (Fig. 3). The melting and crystallization temperatures are shifted gradually to higher values and the shape of the endothermic and exothermic peaks changed, from a very broad maximum to relatively sharp peak, with increasing mass fraction, that is, degree of polymerization of the PBT segments, p (Table III, Fig. 3). The increase in T_m is a consequence of the increasing size of the crystallites and their degree of regularity with increasing p . The multiple peaks which occur in some thermograms indicate the presence of crystallites of different size and perfection due to the irregularity of the length of PBT segments or due to the effect of crystal reorganization which occurs during heating. This results in the appearance of a small exo- and endo-peaks before the main melting peak.^{15-18,28-31}

The melting and crystallization thermograms (Fig. 3) were used to calculate the corresponding heat effects, ΔH_m and ΔH_c (Table III). The values of ΔH_m and $|\Delta H_c|$ shift to higher values with increasing mass fraction of PBT segments in the copolymer. In the second scans, the enthalpies of melting were

TABLE III
DSC Results for the Poly(ester-ether-siloxane)s and PBT Homopolymer

Sample	T_m^a , °C	ΔH_m^a , J g ⁻¹	T_c , °C	ΔH_c , J g ⁻¹	ΔT_h ($T_m - T_c$), °C	$w_c^{\text{DSC } a}$, %	$w_c^{\text{PBT } a}$, %	$w_c^{\text{WAXS } b}$, %
PBT	227 (225)	46.8 (46.2)	191	-66.9	36	32.4 (32.0)	32.4 (32.0)	64
TPEES-10	223 (222)	40.6 (40.5)	184	-59.4	39	28.1 (28.0)	30.0 (29.9)	54
TPEES-20	222 (221)	29.4 (31.6)	180	-54.3	42	20.3 (21.8)	24.0 (25.8)	46
TPEES-30	222 (220)	27.0 (26.9)	175	-42.0	47	18.7 (18.6)	25.5 (25.4)	45
TPEES-40	223 (220)	22.9 (22.3)	173	-37.6	50	15.8 (15.4)	25.1 (24.5)	37
TPEES-50	216 (215)	14.0 (13.4)	161	-18.4	56	9.7 (9.3)	18.2 (17.5)	28
TPEES-60	214 (213)	16.1 (13.3)	167	-14.2	47	11.2 (9.2)	25.6 (21.1)	26

^a In parentheses are the values from second heating.

^b Degree of crystallinity determined using WAXS analysis.

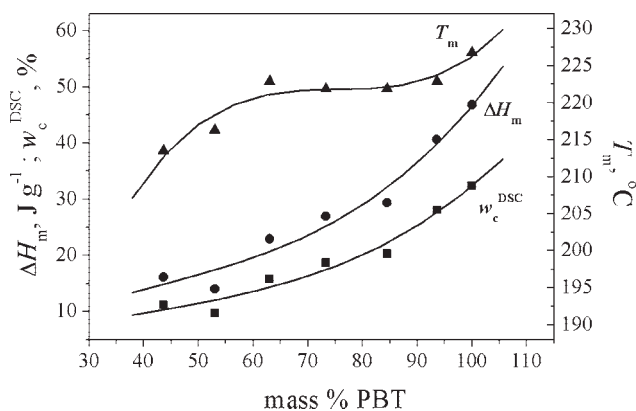


Figure 4 Change in enthalpy of melting (ΔH_m), degree of crystallinity (w_c), and temperature of melting (T_m) with mass fraction of PBT segments.

smaller than in the first scans (with exception of TPEES-20), which indicates a decrease in the degree of crystallinity of the TPEESs. The ratio of the measured ΔH_m of the TPEES sample to the melting enthalpy of completely crystalline PBT homopolymer ($\Delta H_m^0 = 144.5 \text{ J g}^{-1}$)⁶ gave the total DSC degree of crystallinity, that is, the mass fraction of crystallites in the TPEESs, w_c^{DSC} . The ratio of the total degree of crystallinity and the mass fraction of PBT segments determined by ¹H-NMR spectroscopy (w_{PBT} , Table I) gave the mass fraction of hard segments incorporated into the crystallites, w_c^{PBT} .

The obtained results show that ΔH_m increases ($14.0\text{--}40.6 \text{ J g}^{-1}$, in the first scan) with increasing mass fraction of PBT segments. The total degree of crystallinity, w_c^{DSC} , was in the range from 9.7 to 28.1% (in the first scan) and depended on the mass fraction of PBT segments, as well as ΔH_m (Fig. 4). The degrees of crystallinity w_c^{PBT} , which were calculated taking into account the mass fraction of the PBT segments in the TPEESs, were in the range from 18.2 to 30.0%. This means that 18–30 mass % of the PBT segments in the TPEES samples crystallized. The degree of crystallinity of the PBT homopolymer was: $w_c = w_c^{\text{PBT}} = 32.4\%$. These results indicated that the hard segments in the TPEES could not crystallize completely and that some of short PBT segments were incorporated into the amorphous phase. This was in agreement with earlier results^{15–18} and with the results for thermoplastic poly(ester-ether)s.^{27,30,32}

PBT homopolymer is a fast-crystallizing polymer. By comparing the supercooling, that is, the difference between the melting and crystallization temperature, it is possible to analyze the rate of crystallization of differently segmented copolymers. PBT homopolymer has a supercooling of 36°C (Table III). The supercooling of the hard segments ($\Delta T_h = T_m - T_c$) of the synthesized poly(ester-ether-siloxane)s was in the range from 39 to 56°C , indicating that the rate of crystallization of the TPEES was lower than that

of PBT, because of the presence of the soft EO-PDMS-EO segments (Table III). The results show that the crystallization rates of the TPEESs decreased with increasing mass fraction of EO-PDMS-EO segments.

The glass transition temperature of the poly(ester-ether-siloxane)s was determined from the loss modulus peak temperature G''_{peak} of dynamical mechanical measurements performed in temperature range from room to 170°C . The glass transition temperatures, T_g s, of the amorphous phase in the poly(ester-ether-siloxane)s were between $+25$ and $+45^\circ\text{C}$ (Table V). PBT homopolymer has a glass transition temperature of $+53^\circ\text{C}$, which is higher than the T_g values of the TPEESs, which indicates mixing of the amorphous hard PBT segments with the soft EO-PDMS-EO segments. The T_g values of the TPEESs decreased with increasing content of soft segments. It was reported that pure EO-PDMS-EO copolymer formed a two-phase morphology and exhibited two glass transitions at -105 and -8°C . The lower temperature transition can be assigned to the principal PDMS segments and the second one to the end-group segment. End-group segments due to significant difference in chemical structure with PDMS are segregated and form a separate phase.³³ We have previously reported that similar poly(ester-ether-siloxane)s exhibit the glass transition temperatures of the amorphous PDMS phase were between -127.5 and -114.5°C , which is close to the PDMS homopolymer and is also dependant on the content of the hard PBT segments.^{17,18}

WAXS analysis of the poly(ester-ether-siloxane)s

The synthesized poly(ester-ether-siloxane)s were characterized by the WAXS method and the percents of crystallinity, w_c^{WAXS} , obtained from the diffractograms (Fig. 5), are presented in Table III.

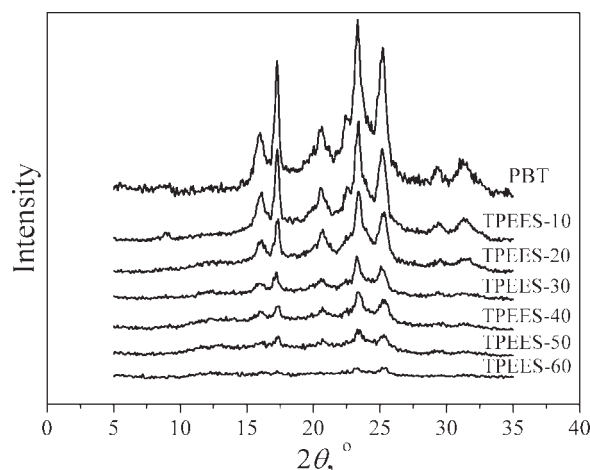


Figure 5 X-ray diffractograms of the TPEESs and PBT homopolymer.

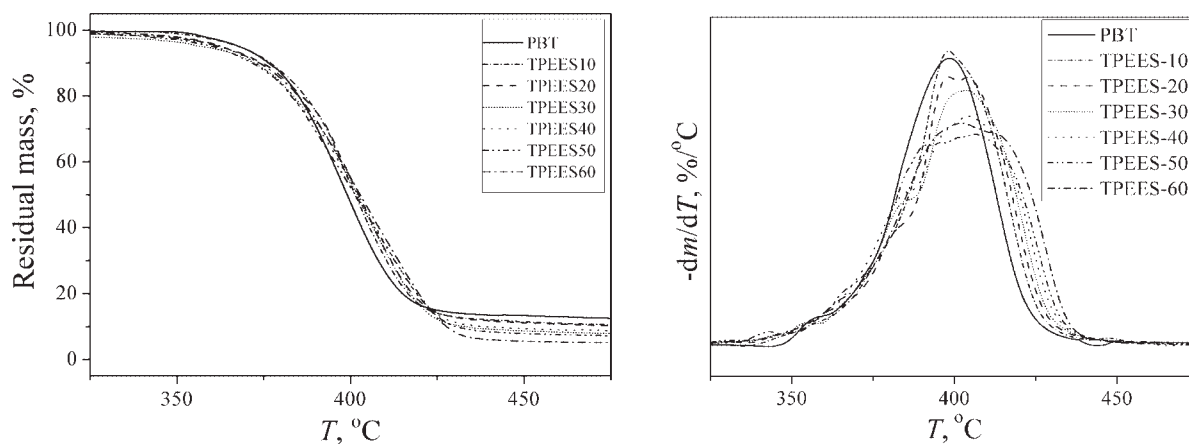


Figure 6 TG and DTG curves for TPEES and PBT homopolymer in nitrogen.

For the PBT homopolymer, two crystal modifications (α - and β -form) have been described, and their crystal structures were analyzed by X-ray diffraction.³⁴ The transition between the two modifications occurs reversibly by mechanical deformations: from the α -form to the β -form by elongation and inversely by relaxation. The primary modification is the α -form which belongs to the triclinic system, with unit cell parameters: $a = 4.83 \text{ \AA}$, $b = 5.94 \text{ \AA}$, c (fiber axis) $= 12.95 \text{ \AA}$, $\alpha = 99.7^\circ$, $\beta = 115.2^\circ$, and $\gamma = 110.8^\circ$.

The positions of the peak maxima in the diffractogram of the PBT homopolymer, synthesized in a similar way as the series of TPEES, were situated at the following 2θ values: 16.12, 17.40, 20.68, 23.32, and 25.24°, which are very similar to the literature data. The diffractograms of TPEES were very similar to the diffractograms of the PBT homopolymer. The main peaks in the TPEES diffractograms occurred at almost the same 2θ values as those of the PBT homopolymer. Hence, it could be concluded that all the TPEES samples crystallized in the α -form. However, the areas of the crystalline peaks of the TPEES were reduced compared with the peaks from PBT. In the TPEES diffractograms, a amorphous halo due to the presence of the PDMS-block was also observed.

The degrees of crystallinity, w_c^{WAXS} , were in the range from 26.0 to 54.0% (Table III), whereas the degree of crystallinity of the PBT homopolymer was 64.0%. The

calculated w_c^{WAXS} is the total degrees of crystallinity, which could be compared with the total DSC degrees of crystallinity. The WAXS degrees of crystallinity increased with increasing mass fraction of PBT segments, very similar to the DSC degrees of crystallinities. The w_c^{WAXS} values demonstrate that the total degree of crystallinity in the copolymers almost exclusively depends on the mass fraction of hard segment.

TG analysis of the poly(ester-ether-siloxane)s

The thermal stability and degradation behavior of the synthesized TPEES were investigated by TGA in a nitrogen atmosphere and compared to the behavior of the PBT homopolymer.¹⁶ The obtained results are shown in Figure 6 and Table IV.

The TG curves show that the thermal behavior of all samples was very similar and that the mechanism of degradation is complex. The degradation of the TPEES samples commences between 357 and 368°C, whereas the degradation of the PBT homopolymer starts at 368°C ($T_{5\%}$ mass loss). The composition of the TPEES samples did not significantly influence their degradation behavior in nitrogen. Almost all the TPEES samples started to lose mass at a lower temperature compared to PBT because of the presence of weak ether bonds from ethylene oxide units, which connect the soft and hard PBT

TABLE IV
Thermal Gravimetric Analysis of the TPEESs and PBT Homopolymer in Nitrogen

Sample	Temp. for 5% mass loss, °C	Temp. for 50% mass loss, °C	Temp. for max rate of degradation, °C	Residual mass at 500°C, %
PBT	368	399	399	12.0
TPEES-10	368	401	399	9.9
TPEES-20	362	402	383/398/405	9.7
TPEES-30	357	402	385/403	7.3
TPEES-40	362	402	385/404/407	8.3
TPEES-50	360	401	391/396/402/406	6.8
TPEES-60	363	403	403/412	4.7

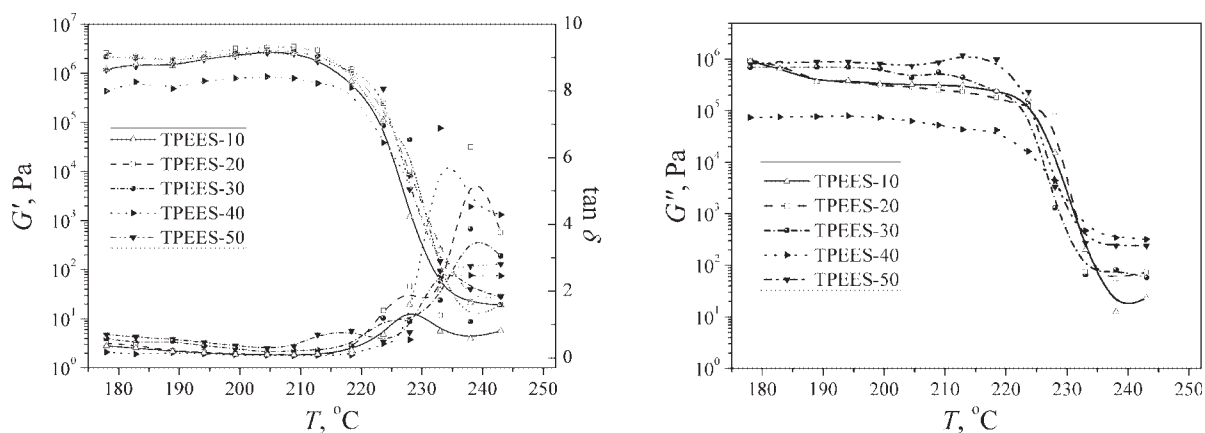


Figure 7 Storage (G'), loss (G'') shear modulus and $\tan \delta$ of the TPEESs versus temperature at 6.31 rad s^{-1} .

segments. The synthesized TPEESs commenced to degrade before the PBT homopolymer, but the copolymer degradation very quickly becomes slower than the degradation of the PBT homopolymer (Fig. 6). The slower copolymer degradation is the consequence of the presence of poly(dimethylsiloxane) chains. The residual masses of the TPEES samples at 500°C ranged from 4.7 to 9.9 %, whereas the residual mass of the PBT homopolymer at 500°C was 12.0%. The residual mass in nitrogen originated mainly from the PBT fraction and this behavior could be explained by the mechanism of degradation of poly(dimethylsiloxane) chains in a nitrogen atmosphere,³ which occurs after disruption of the ether bonds between the hard and the soft segments. In a nitrogen atmosphere, degradation occurs through depolymerization, with the formation of cyclosiloxanes, which are thermally more stable than linear poly(dimethylsiloxanes), and because of this the residual masses were very small.

Rheological behavior of the poly(ester-ether-siloxane)s

The viscoelastic properties of the TPEES are presented as mechanical spectra by following the dependence of the storage (G') and loss (G'') shear

moduli and $\tan \delta$ (Fig. 7) versus temperature at a frequency of 6.31 rad s^{-1} .

The temperature dependence of the storage modulus, the loss modulus, and $\tan \delta$ shows three regions of viscoelastic behavior: a rubbery plateau, a transition from the rubbery plateau to the flow region, and a flow region. In the rubbery plateau region, the storage and the loss moduli were relatively constant, that is, independent of changing the temperature. A rubbery plateau region is characteristic for chemically or physically crosslinked polymers and also for amorphous polymer of high molar mass. The two-phase microstructure of the thermoplastic elastomers is responsible for the appearance of the rubbery plateau region. The storage modulus [G' (45°C) = 8.7×10^6 – $5.6 \times 10^8 \text{ Pa}$, Table V] increased with increasing mass fraction of the hard PBT segments, that is, with increasing rigidity of the copolymer chains. Also, the results showed that G' in a rubbery plateau region increased with increasing the total degree of crystallinity (Fig. 8). The viscoelastic parameter of importance for TPEESs is the crossing temperature $T_{G'=G''}$ at which G' is equal to G'' , i.e., $\tan \delta = 1$. Below the crossing temperature, the behavior of the TPEESs is mainly elastic, i.e., $G' > G''$, and above this temperature the behavior changes to viscous ($G'' > G'$). The crossing temperature, which corresponds to the interval of the melting

TABLE V
Storage (G'), Loss (G''), Shear Modulus, Crossing Temperature ($T_{G'=G''}$), and Microphase Separation Transition Temperature (T_{MST}) of the TPEESs

Sample	$T_g G''_{\text{peak}}$	G' (45°C), Pa	G' (190°C), Pa	G'' (190°C), Pa	$T_{G'=G''}$, $^\circ\text{C}$	T_{MST} , $^\circ\text{C}$	Interval of melting (DSC)
TPEES-10	45	5.6×10^8	1.8×10^6	3.7×10^5	230	240	210–235
TPEES-20	45	4.1×10^8	1.7×10^6	3.7×10^5	233	233	214–235
TPEES-30	39	3.8×10^8	1.3×10^6	7.0×10^5	227	232	214–235
TPEES-40	35	1.7×10^8	4.8×10^5	7.8×10^4	230	235	214–235
TPEES-50	34	7.9×10^7	1.6×10^6	8.9×10^5	228	233	210–225
TPEES-60 ^a	25	8.7×10^6	2.9×10^4	4.1×10^3	151	171	205–225

^a G' and G'' —determined at 130°C , as TPEES-60 at 190°C was in molten state.

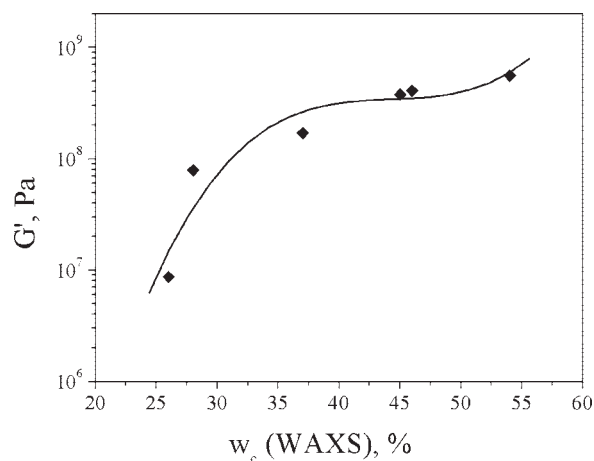


Figure 8 Storage (G') modulus at 45°C versus total degree of crystallinity determined by WAXS analysis.

process determined by DSC, ranged from 151 to 233°C. The value of the storage modulus at 190°C ranged from 4.8×10^5 to 1.8×10^6 Pa and the loss modulus from 7.8×10^4 to 8.9×10^5 Pa. The sample TPEES-60 with the highest content of soft segments exhibited the beginning of the melting process at 151°C and at 190°C it was completely in molten state. Another important parameter for microphase-separated copolymers, such as poly(ester-ether-siloxane)s, is the microphase separation transition temperature, T_{MST} (or order-disorder transition).^{35–37} Size of the PBT crystallites begins to decrease when the temperature is increased above a certain critical value, and the ordered microdomain structure changes to a disordered homogeneous melt at T_{MST} (isotropic melt). This temperature for TPEESs was determined from Han's diagrams (plots of $\log G'$ vs. $\log G''$, Fig. 9). The Han's diagrams show that the microstructure transformations were manifested by changes in the shape and slope of the curves G' versus G'' as the temperature is increased. At T_{MST} and above that temperature, the $\log G'$ versus $\log G''$ plots cease to vary with temperature. In the other words, T_{MST} is the lowest temperature at which the polymer melt is isotropic. The microphase separation transition temperatures for the investigated TPEESs,

depending on composition of the copolymers, were in the range from 171 to 240°C (Table V).

In comparison with poly(ester-siloxane)s based on carboxypropyl-terminated PDMS (TPES), the TPEESs showed higher inherent viscosities, higher melting temperatures, higher thermal stability, and better mechanical properties. The rate of crystallization and the degrees of crystallinity were lower in the TPEES than in the TPES series because of the presence of the soft ethylene oxide-siloxane segments.

The combination of the properties of PBT and PDMS makes these block copolymers excellent candidates for surface modifying additives, drug encapsulation, and biomaterial applications. For example, by changing the copolymer composition, the mechanical and surface characteristics of the poly(ester-ether-siloxane)s can be tailored and adjusted to the requirement for medical application, such as films and microspheres in controlled drug release.

CONCLUSIONS

A series of novel TPEESs with different mass ratio of hard to soft segments were synthesized by two-step melt transesterification of DMT with BD and α,ω -dihydroxy-(EO-PDMS-EO) ($\bar{M}_n = 1200 \text{ g mol}^{-1}$). The composition of the poly(ester-ether-siloxane)s, obtained on the basis of $^1\text{H-NMR}$ analysis, showed that the content of soft segments in the copolymers was close to the composition of the feed. Extraction with chloroform showed that both the soluble and insoluble fractions had multiblock structure.

The TPEES copolymers were semicrystalline polymers. The degree of crystallinity, the melting and crystallization temperatures of the TPEES increased with increasing mass fraction of the hard PBT segments. The X-ray diffraction analysis confirmed that in the TPEES the hard PBT segment crystallized in a threeclinic crystal lattice, that is similar to PBT homopolymer. The thermal stability of the TPEESs was lower in comparison with the PBT homopolymer, because of the presence of ether bonds in soft segments, but the copolymers degraded slower.

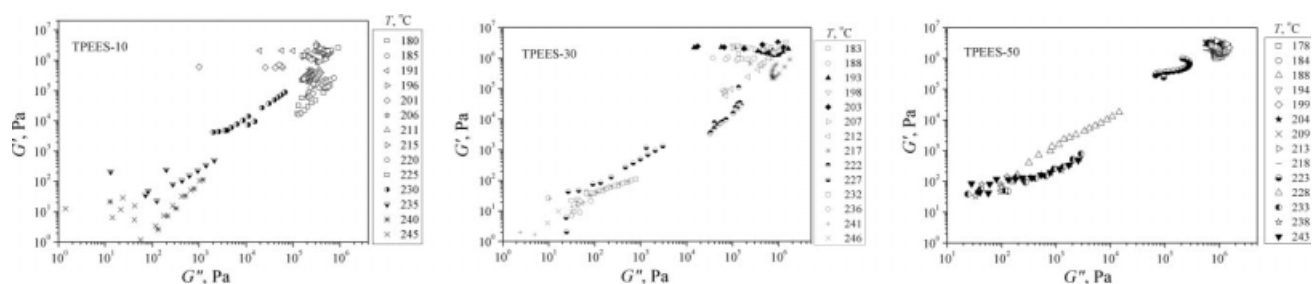


Figure 9 Log G' versus log G'' for the TPEES-10, TPEES-30, and TPEES-50 samples at different temperature (Han's diagram).

The results showed that the storage modulus of the copolymers in a rubbery plateau region increased with increasing total degree of crystallinity. The rheological measurements of TPEESs showed that the microphase separation transition temperatures were in the range from 171 to 240°C.

It can be concluded that the inclusion of the siloxane prepolymer with terminal EO units resulted in slightly improvement of miscibility of the reaction mixture and therefore to better thermal and mechanical properties. However, the usage of a prepolymer with larger EO sequences in the synthesis of TPEES might probably improve compatibility in the reaction mixture and result in higher molecular weight polymers, as well as in better homogeneity and mechanical properties. Also, the mechanical and surface characteristics of the poly(ester-ether-siloxane)s can be tuned by changing the copolymer composition and adjusted to the requirement for medical application.

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