

Synthesis of thermoplastic poly(ester-siloxane)s in the melt and in solution

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Abstract: Two series of thermoplastic elastomers, based on poly(dimethylsiloxane), PDMS, as the soft segment and poly(butylene terephthalate), PBT, as the hard segment, were synthesized by catalyzed transesterification, from dimethyl terephthalate, DMT, silanol-terminated poly(dimethylsiloxane), PDMS-OH, $\bar{M}_n = 1750$ g/mol, and 1,4-butanediol, BD. The mole ratio of the starting comonomers was selected to result in a constant hard to soft weight ratio of 55:45. The first series was synthesized in order to determine the optimal mole ratio of BD and DMT for the synthesis of high molecular weight thermoplastic poly(ester-siloxane)s, TPESs. The second series was performed in the presence of the high-boiling solvent, 1,2,4-trichlorobenzene in order to increase the mixing between the extremely non-polar siloxane prepolymer and the polar reactants, DMT and BD, and, therefore, avoid phase separation during synthesis. The structure and composition of the synthesized poly(ester-siloxane)s were verified by ¹H-NMR spectroscopy, while the melting temperatures and degree of crystallinity were determined by differential scanning calorimetry (DSC). The effectiveness of the incorporation of the silanol-terminated poly(dimethylsiloxane) into the polyester chains was verified by chloroform extraction. The rheological properties of the poly(ester-siloxane)s were investigated by dynamic mechanical spectroscopy (DMA).

Keywords: poly(ester-siloxane)s, thermoplastic elastomers, silanol-terminated poly(dimethylsiloxane)

INTRODUCTION

Thermoplastic elastomers are an important category of engineering materials because they frequently have extraordinary combinations of physical properties, such as elasticity, low-temperature flexibility, impact strength, toughness and ease

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of processing (extrusion, injection molding, *etc.*). Block copolymers belonging to the class of thermoplastic elastomers consist of two types of chemically incompatible segments, *i.e.*, hard-crystalline and soft-amorphous segments, and show a phase-separated microstructure. Micro-domains rich in hard-segments, resulting from intermolecular actions (*e.g.*, crystallization, hydrogen bonds) from so-called physical crosslinks and guarantee good mechanical strength, while the soft amorphous matrix improves the flexibility. The properties of thermoplastic elastomers depend on the type and nature of the hard and soft segments, and also on their mass ratio and respective lengths.^{1,2}

Poly(organosiloxane) containing multiphase copolymers have been extensively studied and described frequently in the literature. Polycondensation is the most versatile technique for the synthesis of such block or segmented copolymers. This is mainly due to the availability of a wide variety of well-defined reactive telechelic siloxane oligomers.³ Poly(organosiloxane)s exhibit many important and interesting properties. Although possessing a very low glass transition temperatures, these polymers are able to maintain thermal stability over a wide temperature range in both inert and oxidizing environments. Furthermore, these materials are resistant to UV radiation, ozone and atomic oxygen. Low surface tension, low surface energy, physiological inertness and high gas permeability are only a few of the many other interesting properties exhibited by these materials. These physical properties are relatively unaffected by temperature.^{3,4} As a result of the described unique combination of the properties of poly(organosiloxane)s, siloxane containing block or segmented copolymers have received special attention for applications such as biomaterials, photoresists, gas separation membranes, protective coatings, elastomers and emulsifiers.³

A number of copolymers based on poly(butylene terephthalate) (PBT) hard segments and low molecular weight soft segments consisting of various poly(dimethylsiloxane)s (PDMS), and polyethers have been synthesized using the so-called catalyzed two-step transesterification reaction in the melt.^{5–14} Poly(butylene terephthalate) has high structural regularity, it crystallizes rapidly and has a high degree of crystallinity.^{15,16} As a result of its rapid crystallization, PBT is very suitable for use as the hard segment in segmented copolymers. The incorporation of poly(organosiloxane)-segments into a PBT-backbone results in improved clarity, surface smoothness and non-sticking properties, as well as good film, fiber and hydrophobic properties of the resulting copolymers.^{17–22} In order to incorporate effectively poly(organosiloxane)-segments into a polyester-backbone, the most common approach has been to endcap the poly(organosiloxane) with terminal silanol,^{5,6,9,10,12} hydroxyalkyl,^{17–22} carbohypropyl^{12–14} or aminopropyl⁸ groups, and also various poly(organosiloxane)-polyether copolymers with hydroxyl end groups.^{5–7,11}

In previous papers,^{12–14} the synthesis, structure and properties of different thermoplastic poly(ester-siloxane)s, TPESs, based on PBT as the hard segment and PDMS

as the soft segment were described. The obtained TRESs differed in: 1) the functionality of the end-terminated poly(dimethylsiloxane)s (*i.e.*, either silanol- or carboxypropyl-) which were incorporated into the polyester-backbone as flexible segments,¹² 2) the length of the carboxypropyl-terminated PDMS prepolymers with a constant mass ratio of the hard and soft segments¹³ and 3) the mass ratio of the hard and soft segments with a constant length of the carboxypropyl-terminated PDMS prepolymer.¹⁴

In the present work, two series of thermoplastic poly(ester-siloxane)s based on a silanol-terminated PDMS prepolymer were prepared in the melt and in solution of 1,2,4-trichlorobenzene. The first series was prepared in order to optimize the polymerization conditions in the melt and second one in solution with the intention of improving the compatibility of the reaction mixture and, therefore, the effectiveness of the incorporation of poly(dimethylsiloxane) into the polymer chains. Thermoplastic poly(ester-siloxane)s were synthesized by catalyzed transesterification, from dimethyl terephthalate, DMT, 1,4-butanediol, BD, and silanol-terminated poly(dimethylsiloxane), PDMS-OH. The catalyst was tetra-*n*-butyl-titanate, Ti(OBu)₄. The first series was prepared by reaction in the melt, with the mass ratio of hard to soft segments in the reaction mixture constant at 55/45. In this series, the influence of the mole ratio of BD and DMT (varied in the range from 1.2 to 2.2), was investigated in order to determine the optimal ratio for TPES synthesis. In the second series, the effect of the amount of added solvent (1,2,4-trichlorobenzene) on the inherent viscosity of the prepared TPESs was investigated, at the optimal BD/DMT molar ratio of 1.4. Phase separation during the synthesis of segmented copolymers can be avoided either by the addition of an appropriate solvent^{24,25} or by using siloxane-containing triblock prepolymers with hydrophilic terminal blocks, such as poly(ethylene oxide) (PEO), when the terminal blocks serve as a compatibilizer between the extremely non-polar PDMS and the polar DMT and BD.¹¹ In this work, it was decided to use a solvent to improve the mixing of the reactants and to increase the incorporation of PDMS-OH on the PBT chains, as well as to increase the molar mass of the synthesized copolymers. The effect of the structure and size of the synthesized poly(ester-siloxane)s on their thermal and rheological properties was determined by differential scanning calorimetry (DSC) and by dynamic mechanical spectroscopy (DMA).

EXPERIMENTAL

Reagents

α,ω -Disilanol-poly(dimethylsiloxane) (PDMS-OH), from ABCR (Germany), was dried over molecular sieves before use. The number-average molar mass of the PDMS-OH, as determined by vapor pressure osmometry, was 1750 g/mol. Dimethyl terephthalate (DMT) was purified by recrystallization from absolute ethanol and dried at 80 °C for 24 h before use. 1,4-Butanediol (BD), 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) and 1,2,4-trichlorobenzene (from Merck) were used as received.

Poly(ester-siloxane) synthesis

The thermoplastic poly(ester-siloxane)s of the first series (TPES 1-7M, Table I) were synthesized by a catalyzed two-step reaction involving transesterification and polycondensation in the melt. The amounts of the individual reactants were fixed according to the following considerations: DMT and PDMS-OH in order to obtain a constant mass ratio of hard to soft segments (55/45) in the copolymer products, while the molar BD/DMT ratio was varied in the range from 1.2 to 2.2. The amount of thermal stabilizer, DPPD, was 0.5 mass % in the starting reaction mixture, while the amount of catalyst, Ti(OBu)₄, was 1.0 mmol per mol of dimethyl terephthalate. It was also found that the catalyst should be added in two portions: 60 mass % at the beginning of the reaction, and the remaining 40 mass %, together with the thermal stabilizer, when the second reaction step was commenced.^{12,23}

TABLE I. Reaction mixture compositions for the syntheses of the TPESs

Sample	mol BD/mol DMT	MeOH/%
Series I, syntheses in the melt		
TPES-1M	2.20	88.2
TPES-2M	1.55	83.1
TPES-3M	1.45	83.1
TPES-4M	1.40	83.1
TPES-5M	1.35	78.1
TPES-6M	1.30	78.1
TPES-7M	1.20	68.0
Series II, syntheses in solution		
TPES-1S	1.40	87.2
TPES-2S		89.7
TPES-3S		89.7

The starting reaction mixture (*e.g.*, for TPES-4M: 0.0981 mol of DMT, 0.1373 mol of BD, 0.0086 mol of PDMS-OH and 0.06 mmol of catalyst) was charged into a reactor at room temperature and then heated under nitrogen at atmospheric pressure for approximately 2.0–2.5 hours. The first step, transesterification, was carried out from 160 to 240 °C, when the methanol was distilled off. After the first step, DPPD stabilizer (0.232 g) and the second portion of catalyst (0.04 mmol) were added and vacuum was applied. The reaction mixture was kept at 250 °C, under vacuum < 1 mm Hg, for 3.0 h. Finally, the obtained viscous slurry was allowed to cool to ambient temperature in the reactor under nitrogen.^{12,23}

The thermoplastic poly(ester-siloxane)s of the second series (TPES 1-3S, Table I) were synthesized in a solution of 1,2,4-trichlorobenzene^{23–25} 10 mass % (TPES-1S) 25 mass % (TPES-2S) and 50 mass % (TPES-3S) of solvent in the reaction mixture). The reaction mixture compositions were in all cases the same as for the synthesis of sample TPES4 in the first series, and the reaction conditions were also the same. The synthesis in solution differed from the synthesis in the melt in that a reduced pressure of 12–15 mm Hg (water vacuum pump) was applied after the transesterification, to remove the solvent. Subsequently, a vacuum oil pump was used and a pressure lower than 1 mm Hg was applied, as in the first series.

Soxhlet extraction of the TPES-samples

The synthesized TPES samples, weight about 0.15 g, were extracted with 100 cm³ of chloroform in a Soxhlet apparatus for seven days.¹¹ The extracted and insoluble fractions were dried for

five hours at 100 °C. The dry soluble and dry insoluble fractions were weighed and the samples were analyzed by $^1\text{H-NMR}$ spectroscopy in order to determine the composition of the copolymers.

Characterization of the TPES samples

$^1\text{H-NMR}$ (200 MHz) spectra of the TPESs were obtained on a Varian Gemini-200 instrument using their solutions in CF_3COOD . The solvent was simultaneously used as the internal standard.

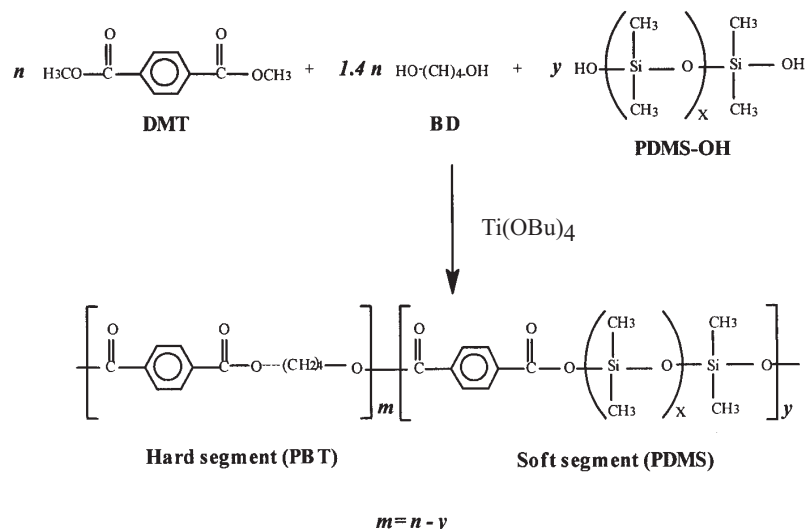
The inherent viscosities, η_{inh} , of the TPESs were measured in a mixture of phenol/trichloroethylene/toluene (1:1:2 vol.) at 30 °C, using an Ubbelohde viscometer. The concentration of the copolymer in the solution was 0.5 g/dl.

The rheological measurements of the TPESs melts (η^* , G' , G''), was performed using a Rheometrics Mechanical Spectrometer RMS-605, operating in the dynamic shear mode between two parallel plates in the temperature range 180–240 °C. The frequency was varied from 0.1 to 100 rad/s. The radius of the samples was 25 mm and the thickness about 1.0 mm. The samples were prepared by press molding at 250 °C.

Differential scanning calorimetry (DSC) was performed using a Perkin–Elmer DSC-2 thermal analyzer. The DSC scans were recorded between 50 and 250 °C under a dynamic nitrogen atmosphere (flow rate $25 \text{ cm}^3/\text{min}$) at a heating and cooling rate of 10 °C/min (two scans were run for each sample). The weight of the samples was approximately 10 mg. From the scans, the melting point (T_m) and the crystallization point (T_c) of the hard segment were determined.

RESULTS AND DISCUSSION

The synthesis of the thermoplastic poly(ester-siloxane) copolymers is shown in Scheme 1:



Scheme 1. Synthesis of thermoplastic poly(ester-siloxanes).

Two series of thermoplastic poly(ester-siloxane)s, TPESs, were synthesized by a catalyzed two-step reaction, involving transesterification and polycondensation. TPES samples of the first series were prepared in the melt, while the samples of the second series were prepared in a solution of 1,2,4-trichlorobenzene. In the case of the first series, the first reaction step, transesterification of dimethyl terephthalate with 1,4-butanediol and PDMS-OH, was carried out in the melt, in

the temperature range 160 – 240 °C, at normal pressure in the presence of $\text{Ti}(\text{O}i\text{Bu})_4$ catalyst. During the first step, butylene terephthalate-oligomeric esters were formed. After most of the methanol (80 – 90 %, Table I) had been distilled off, the second, polycondensation step was carried out under reduced pressure. The polycondensation was performed by heating the mixture to 250 °C to remove the excess 1,4-butanediol and, hence, to obtain high molar mass copolymers. In the case of the second series (syntheses in solution), after the transesterification, reduced pressure of a water vacuum pump was applied to remove the solvent and subsequently, a vacuum oil pump was used in order to reduce the pressure to below 1 mm Hg, as in the first series. *N,N'*-Diphenyl-*p*-phenylenediamine, DPPD, a heat stabilizer, was used in both series to protect the polymer chains from thermal degradation during the polycondensation reaction at 250 °C.

Viscosities of the synthesized TPESs

The compositions of the starting reaction mixtures were selected to result in copolymers with a constant hard-to-soft mass ratio of 55/45 in both series, while the molar mass of the employed PDMS-OH was 1750 g/mol. In the first series, mole ratio of the reacting –OH groups from BD and –COOCH₃ groups from DMT was varied from 1.2 to 2.2, in order to determine the optimal ratio for the synthesis of TPES copolymers. Poly(ester-siloxane)s are not soluble in common organic solvents, such THF or chloroform, which are usually used for GPC.¹² Therefore, as an indicator of the molar masses of the prepared copolymers, the inherent (η_{inh}) and the complex dynamic viscosity (η^*), which are given in Table II, were used. The inherent viscosities of the TPESs, determined in a solvent mixture of phenol/trichloroethylene/toluene, were between 0.34 and 0.54 dl/g in the first series. It can be seen that the inherent viscosity increases from 0.34 to 0.54 with increasing mole BD/DMT ratio and then decreased to 0.36, showing a pronounced maximum at a mole BD/DMT ratio of 1.4 (Table II, Fig. 1). It can be concluded that the optimal BD/DMT ratio was 1.4, in which case a copolymer with the highest viscosity of 0.54 dl/g (TPES-4M), was obtained.

TABLE II. Inherent and melt viscosities of the synthesized TPESs and their chemical composition calculated from their ¹H-NMR spectra

Sample	η_{inh}^1 /(dl/g)	η^* (1 Hz) 235 °C/Pa s	mass % of PBT segments	m^2
Series I, syntheses in the melt				
TPES-1M	0.36	30	65.0	15.9
TPES-2M	0.43	40	60.2	12.9
TPES-3M	0.46	50	59.5	12.5
TPES-4M	0.54	170	56.9	11.3
TPES-5M	0.41	70	60.0	12.9
TPES-6M	0.44	50	58.8	12.2

TABLE II. Continued

Sample	η_{inh}^1 (dl/g)	η^* (1 Hz) 235 °C/Pa s	mass % of PBT segments	m^2
TPES-7M	0.34	-	55.3	10.6
Series II, syntheses in solution				
TPES-1S	0.43	80	62.5	14.3
TPES-2S	0.49	120	56.9	11.3
TPES-3S	0.57	240	55.6	10.7

¹Concentration of the copolymer solution = 0.5 g/dl; ²The degree of polymerization of the hard PBT segments, m (Scheme 1), predetermined by the reaction mixture compositions, was 10.4

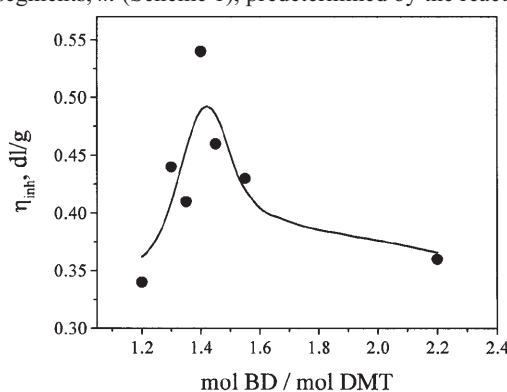


Fig. 1. The inherent viscosity of the TPES samples of series I in dependence on the mole BD/DMT ratio.

The amount of distilled methanol was higher in the second series than in the first one (Table I), *i.e.*, transesterification in solution was more efficient than in the melt. It is well known that the efficiency of transesterification has an effect on the further course of the TPES synthesis, *i.e.*, (on the polycondensation, and, finally, on the molar mass of the obtained copolymer. Due to the high incompatibility of the extremely non-polar PDMS-OH with the polar reactants, DMT and BD, phase separation occurs during the reaction in the melt. It was observed that, when stirring was stopped during the transesterification step, the PDMS-OH floated to the surface of the reaction mixture, hence the reaction mixture was not homogeneous. This problem can be solved by using a high boiling solvent, as 1,2,4-trichlorobenzene, which is a good solvent for both PBT and PDMS-OH at elevated temperatures (above 150 °C).^{24,25} A clear solution was obtained at the synthesis temperature. The effect of the amount of 1,2,4-trichlorobenzene on the inherent viscosity at the optimal BD/DMT ratio of 1.4 was investigated in the second series. The solvent was added in different amounts to the reaction mixture (10, 25 and 50 mass %) in order to improve the mixing of PDMS-OH with DMT and BD, which would result in an increased inherent viscosity, *i.e.*, higher molar mass copolymers.^{23,24} The inherent viscosity increased from 0.43 to 0.57 dl/g on increasing the amount of the solvent from 10 to 50 mass %. From the viewpoint of the molar mass of the synthesized TPESs, the best results were obtained when the amount of the solvent was 50 mass % (TPES-3S).

The complex dynamic viscosity (η^*) shows the same behaviour as the η_{inh} – first it increased with increasing $-OH/-COOCH_3$ mole ratio, showing a maximum at a mole ratio of 1.4 and then decreased in series I, while it increases with increasing amount of solvent in series II (Table II). The recorded changes of the complex dynamic viscosity with temperature and frequency are presented in Fig. 2. From the complex dynamic viscosity measurements, it can be concluded that the synthesized TPES show pseudoplastic behavior over the whole studied temperature range.

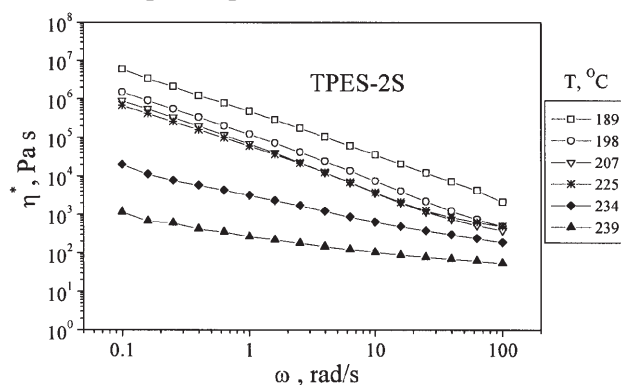


Fig. 2. Complex dynamic viscosity, η^* , versus frequency, at different temperatures for the sample TPES-2S.

Structure of the synthesized TPESs

The molecular structure of the poly(ester-siloxane)s was investigated by 1H -NMR spectroscopy. A typical 1H -NMR spectrum of a TPES is shown in Fig. 3. The spectra gave chemical shifts at 0.39–0.72 ppm of the $Si-CH_3$ protons; at 8.36 ppm of the aromatic protons; at 2.29 and 4.77 ppm of the central and terminal methylene protons of the BD-residue from the hard segments, respectively. The signals of the $-CH_2OH$ or OCH_3 end-groups were absent in the 1H -NMR spectra, indicating that copolymers of high molar masses were obtained. The two main peaks of the $Si-CH_3$ protons at 0.39 and 0.64 ppm indicate that siloxane-equilibration takes place in CF_3COOD and reformation of octamethylcyclotetrasiloxane occurs. The quantity of $Si-CH_3$ protons is the same before and after equilibration in the PDMS-segments and, therefore, has no influence on the calculations based on the 1H -NMR spectra.^{12,13}

The mass fractions of hard, and soft segments, SS, as well as the average degree of polymerization of the hard segments, (m , in Scheme 1), were calculated from the ratio of the integrals of the methylene protons of the BD-residue from the hard segments and the $Si-CH_3$ protons from the soft segments.^{12,23}

$$p_{SS} / (p_{SS} + p_{HS}) = \text{mole fraction of soft segments} = X_{SS}$$

$$1 - X_{SS} = \text{mole fraction of hard segments} = X_{HS}$$

where: p_{SS} = the intensity of 1 proton from SS = the intensity of the $Si-CH_3$ protons signal / 140.43; 140.43 = the number of $Si-CH_3$ protons in the soft segment =

$\bar{X}_n(\text{PDMS-OH}) \times 6 + 12$; $\bar{X}_n(\text{PDMS-OH}) = (\bar{M}_n(\text{PDMS-OH}) - 166) / 74$; $\bar{X}_n(\text{PDMS-OH}) = 21.4 - \text{number average degree of polymerization}$; p_{HS} = the intensity of 1 proton from the HS = the intensity of protons $(b + c)/8$ (Fig. 1)

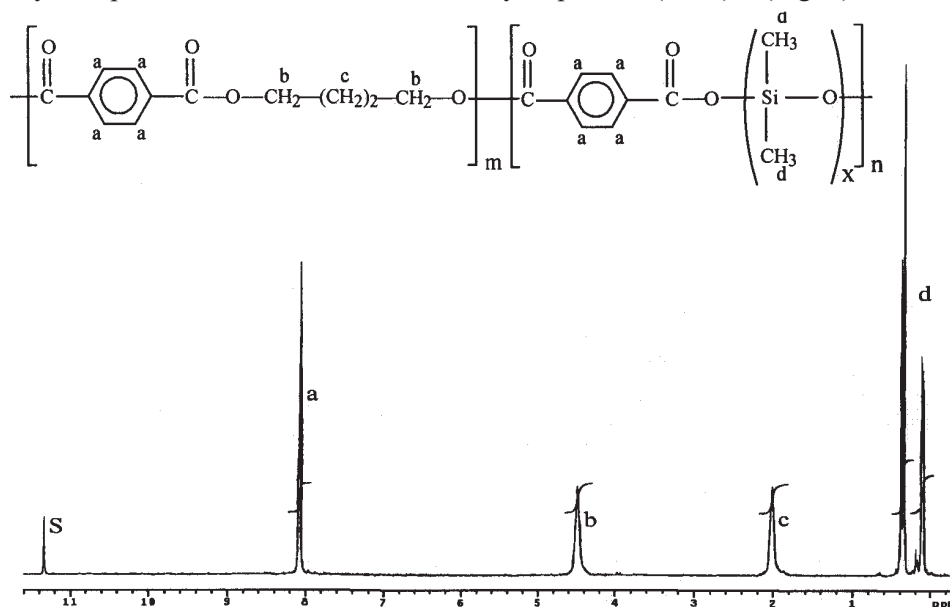


Fig. 3. $^1\text{H-NMR}$ Spectrum of the poly(ester-siloxane) sample TPES-3S.

The mass fraction % of soft segments was calculated in the following manner:

$$\{(X_{\text{SS}} \times M_{\text{SS}}) / (X_{\text{SS}} \times M_{\text{SS}} + X_{\text{HS}} \times M_{\text{HS}})\} \times 100 = \text{mass \% of the soft segment}$$

where: $M_{\text{SS}} = 1880 \text{ g/mol}$ – molar mass of the soft segment PDMS; $M_{\text{HS}} = 220 \text{ g/mol}$ – molar mass of the base unit of the hard segment.

The data obtained from the $^1\text{H-NMR}$ spectra are presented in Table II. The values for the mass fractions of the PBT segments were 53.9–65.0 %, which agree relatively well with the value that was predetermined from the composition of the reaction mixture (55 mass. % PBT). It can be seen in Fig. 4 that the mass fraction of PBT segments in the copolymer increased with increasing BD/DMT ratio.

The average length (degree of polymerization) of the hard PBT segment (m in Scheme 1), calculated from the reaction mixture compositions, was in both series 10.4. The average degree of polymerization of the PBT segments was calculated according to 1 mol of soft PDMS segment ($n = 1$ in Scheme 1). The possibility of $y > 1$ was small, due to the relatively low mole fraction of PDMS-prepolymer in the starting reaction mixtures (2.7 – 3.8 mol %). The average length of the hard segments, calculated from the $^1\text{H-NMR}$ spectra, ranged from 10.6 (TPES-7M) to 15.9 (TPES-1M).

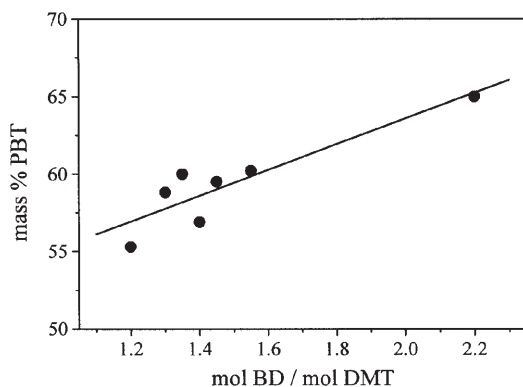


Fig. 4. Mass fraction of the PBT segments in the TPES copolymers of Series I in dependence on the mole BD/DMT ratio.

Analysis of the homogeneity of the synthesized TPESs

The effectiveness of the incorporation of PDMS into the copolymer chains was proven by Soxhlet extraction with chloroform.^{12–14} It is well known that PBT-homopolymers and the block copolymers are insoluble in chloroform, while the PDMS-OH prepolymer and block copolymers with very low PBT content are, however, soluble and, therefore, extractable with chloroform. The results presented in Table III, show that the extracted and insoluble fractions of the examined TPES samples differed in both their composition and structure, containing considerably different amounts of PDMS and PBT segments. The TPES samples lost about 32–37 mass % of their weight during extraction with chloroform. Examination of the extracted and insoluble fractions by ¹H-NMR spectroscopy showed that both contained aromatic rings from the PBT segments and also PDMS segments. The soluble fractions contained 92.5–96.0 mass % of PDMS segments, while the insoluble fractions contained 3.2–11.2 mass % of PDMS segments. The calculated value of m (Scheme 1) in the soluble portion was very small and nearly constant ($m_{\text{sol}} = 0.4\text{--}0.7$), while, on the contrary, in the insoluble portion it was very high ($m_{\text{ins}} = 67\text{--}255$). It can be concluded that both the extracted and insoluble fractions still have a multiblock structure, but with very short PBT blocks in the soluble and very long PBT blocks in the insoluble fractions.

TABLE III. ¹H-NMR analysis of the chloroform soluble and insoluble fractions of the TPESs

Sample	Soluble fraction mass %	Soluble fraction		Insoluble fraction mas %	Insoluble fraction	
		mass % of PDMS	m_{sol} in Scheme 1		mass % of PDMS	m_{ins} in Scheme 1
TPES-4M	32.5	96.0	0.4	67.5	11.2	67
TPES-1S	36.7	93.6	0.6	63.3	6.5	122
TPES-2S	37.0	94.1	0.5	63.0	3.2	255
TPES-3S	37.3	92.5	0.7	62.7	4.6	178

It can be concluded that, in spite of the fact that the reaction was carried out in the presence of a high boiling solvent in order to compatibilize the immiscible

components, phase separation occurred, as was reported by Walch.²⁴ The rather unsatisfactory incorporation of the PDMS segments into the poly(butylene terephthalate) chains and the incomplete homogeneity of the TPESs could be explained by the chemical reactivity of the silanol groups, which prefer to form silanol ethers either with the excess diol present in the reaction mixture or, more likely, with the hydroxyl end groups of the growing polyester chains,¹⁰ as was reported before. Since a longer reaction time (about 6 h at 180 °C)²⁶ is required for the formation of similar ethers, it was not unexpected that incorporation of PDMS-OH through ether linkages was rather poor under the reaction conditions applied in this work.

DSC analysis of the poly(ester-siloxane)s

DSC analysis demonstrated that the synthesized poly(ester-siloxane)s were semicrystalline polymers. The transition temperatures, *i.e.*, melting and crystallization temperatures, of the hard segments were observed by DSC analysis.

The DSC measurements, between 50 and 250 °C, 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 some samples of the poly(ester-siloxane)s. The results are presented in Fig. 5 and Table IV.

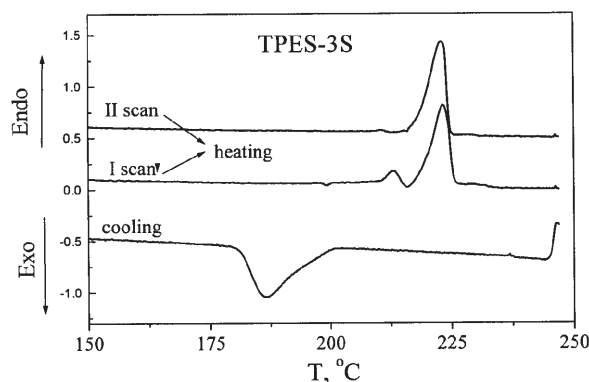


Fig. 5. DSC Curves of the TPES-3S sample obtained during heating and cooling at 10 °C/min.

The DSC curves show high-temperature transitions corresponding to the melting and crystallization temperature of the PBT-segments (Fig. 5). The melting of the crystallites of the TPES samples occurred in the temperature region of 210–225 °C, while crystallization occurred in the region of 180–200 °C. The melting and crystallization temperatures increased with increasing content and length of the hard PBT segments (Table IV). The multiple peaks, which were evident in some of the thermograms, indicate the presence of crystallites of different size and perfection, due to the irregularity of the length of the PBT-segments or due to the effect of crystal reorganization occurring during heating. This results in the appearance of small exo- and endo-peaks before and after the main melting peaks.^{27–30}

TABLE IV. Differential scanning calorimetry (DSC) results for the poly(ester-siloxane)s

Sample	$T_m^a/^\circ\text{C}$	$\Delta H_m^a/(\text{J/g})$	$T_c/^\circ\text{C}$	$\Delta T_h (T_m - T_c)/^\circ\text{C}$	$\Delta H_c/(\text{J/g})$	$w_c \text{ (DSC)}^a/\%$	$w_c^{\text{PBT}} \text{ (DSC)}^a/\%$
TPES-4M	224 (222)	22.4 (21.8)	189	35	-29.8	15.5 (15.1)	26.9 (262)
TPES-1S	224 (223)	25.1 (24.8)	191	33	-35.9	17.4 (17.2)	29.6 (29.2)
TPES-2S	224 (223)	24.2 (25.0)	190	34	-33.4	16.7 (17.3)	31.1 (32.1)
TPES-3S	223 (223)	23.1 (22.6)	187	36	-30.6	16.0 (15.6)	25.9 (25.3)
PBT ^b	225 (224)	51.6 (46.0)	193	32	-54	35.7 (31.8)	35.7 (31.8)

^aIn the brackets are the values from the second run; ^bPBT-homopolymer, synthesized in the same way as sample TPES-4M

The melting and crystallization thermograms (Fig. 5) were used to calculate the corresponding heat effects, enthalpies of melting and crystallization, ΔH_m and ΔH_c , respectively, which also increased with increasing content and length of the hard PBT segments (Table IV). In the second scans, the enthalpies of melting were smaller than in the first scans, except for the sample TPES-2S, which indicate a decrease in the degree of crystallinity of the TPESs. The ratio of the measured ΔH_m of the TPES sample to the melting enthalpy of completely crystalline PBT-homopolymer ($\Delta H_m^\circ = 144.5 \text{ J/g}$)³¹ gave the total DSC-degree of crystallinity, *i.e.*, the mass fraction of crystallites in the TPESs, w_c . The ratio of the total degree of crystallinity and the determined (¹H-NMR) mass fraction of PBT-segments gave the mass fraction of hard segments that were incorporated into the crystallites, w_c^{PBT} :

$$w_c = \Delta H_m / \Delta H_m^\circ \quad \text{and} \quad w_c^{\text{PBT}} = w_c / w_{\text{PBT}}$$

where: ΔH_m is the enthalpy of the melting of the poly(ester-siloxane), $\Delta H_m^\circ = 144.5 \text{ J/g}$ – the enthalpy of the melting of perfectly crystalline PBT-homopolymer, and w_{PBT} – the mass fraction of hard segments in the poly(ester-siloxane), determined by ¹H-NMR spectroscopy.

The total degree of crystallinity (w_c) was in the range of 15.5 to 17.4 % (in the first scan), while the degrees of crystallinity, w_c^{PBT} , which were calculated taking into account the mass fraction of the PBT-segments in the TPESs, were in range from 25.9 to 31.1 %. This means that less than 30 mass % of the PBT-segments in all the TPES samples crystallized. These results show that not all of the hard segments in the TPES could crystallize completely due to their partial incorporation into the amorphous matrix. This is in agreement with earlier results,^{12–14} and also with results described for thermoplastic poly(ester-ether).^{29–32} The obtained results show that w_c and w_c^{PBT} increasing with increasing mass fraction of PBT seg-

ments in the copolymers and also with increasing degree of polymerization of the PBT segments in the chloroform insoluble fractions, m_{ins} (Fig. 6). With increasing mass fraction of PBT segments and m_{ins} , the size of the crystallites increases and consequently w_c and w_c^{PBT} .

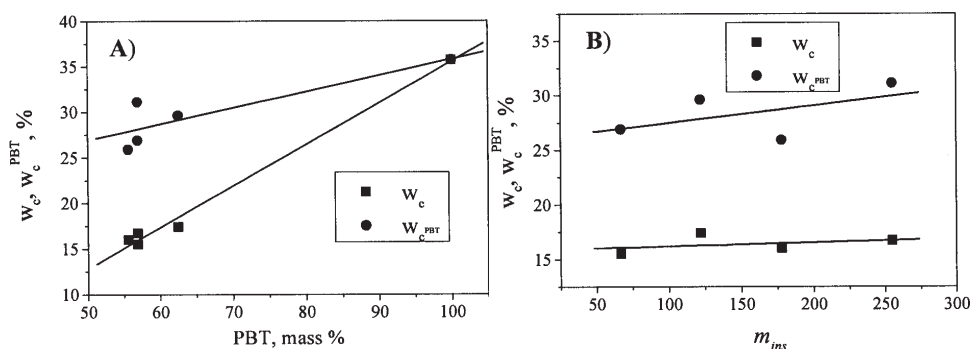


Fig. 6. Degree of crystallinity, w_c and w_c^{PBT} in dependence on the mass % of PBT segments (A) and degree of polymerization of the PBT segments in the chloroform insoluble fractions, m_{ins} (B).

PBT homopolymer is a fast crystallizing polymer. By comparing the supercooling (the difference between the melting and crystallization temperature), it is possible to analyze the rate of crystallization of different segmented copolymers. PBT has a supercooling of 32 °C (Table IV). The supercooling of the hard segments ($\Delta T_h = T_m - T_c$) of the synthesized poly(ester-siloxane)s was in the range 33 to 36 °C, indicating that the rate of crystallization of TPES samples was lower than that of PBT due to the presence of the soft segment (Table IV). The results showed that the crystallization rates of these copolymers were independent of the structure and composition of the synthesized TPESs in the examined range.

Rheological behavior of poly(ester-siloxane)s

The dependence of the storage (G') and loss (G'') shear moduli, $\tan \delta$ and complex dynamic viscosity (η^*) (Fig. 2 and Fig. 8) on temperature and frequency was followed in the rheological measurements. The temperature dependencies of G' , G'' and $\tan \delta$ show two regions of viscoelastic behaviour from 180 to 240 °C, a rubbery region and a flow region (Fig. 7). In the rubbery plateau region, the storage and the loss moduli decrease slowly with temperature due to the incomplete homogeneity of the samples. The rubbery plateau region is characteristic for chemically or physically cross-linked polymers and also for amorphous polymers of high molecular weight. The two-phase microstructure of the thermoplastic elastomers, which is a consequence of the chemical incompatibility of the physically cross-linked hard segments and the amorphous soft segments is responsible for the appearance of the rubbery plateau region.

From Fig. 7, only a transition from the rubbery plateau region to the flow region can be seen for the investigated poly(ester-siloxane)s. The cross-over temper-

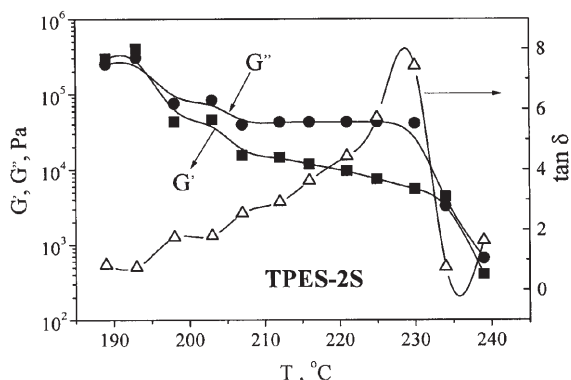


Fig. 7. Storage (G' and loss (G'') shear modulus and $\tan \delta$ of sample TPES-2S in dependence on the temperature, at 6.31 rad/s.

ature, $T_{G'=G''}$, when G' is equal to G'' , *i.e.*, $\tan \delta = 1$, corresponds to the transition from the rubbery to the flow region. Below the cross-over temperature, the behaviour of the poly(ester-siloxane)s is mainly elastic, *i.e.*, $G' > G''$, and above this temperature the behaviour changes to viscous ($G'' > G'$).³³ The cross-over temperature ($T_{G'=G''} = 180 - 194$ °C, Table V), corresponds to the temperature of the onset of the melting process determined by DSC. In the investigated poly(ester-siloxane)s series, the values of the storage modulus at 200 °C were about $(2.5 - 4.3) \times 10^4$ Pa and the loss modulus about $(7.0 - 9.0) \times 10^4$ Pa (Table V). It can be seen that the values of the storage modulus at 190 °C in Series II increased with increasing mass % of PBT segments, *i.e.*, with increasing rigidity of the chains of the copolymer (Tables II and V).

TABLE V. Storage (G'), loss (G'') shear modulus and complex dynamic viscosity at 200 °C, crossing temperature ($T_{G'=G''}$) and microphase separation transition temperature (T_{MST}) of some of the TPES samples

Sample	G' (200 °C)/Pa	G'' (200 °C)/Pa	η_1^* , (200 °C)/Pa s	$T_{G'=G''}/\text{°C}$	$T_{MST}/\text{°C}$
TPES-4M	2.5×10^4	8.8×10^4	1.4×10^4	180	232
TPES-1S	2.5×10^4	9.0×10^4	1.5×10^4	193	236
TPES-2S	4.3×10^4	7.5×10^4	1.5×10^4	194	234
TPES-3S	3.1×10^4	7.5×10^4	1.3×10^4	186	235

An important rheological parameter for phase segregated copolymers, such as poly(ester-siloxane)s, is the microphase separation transition temperature, T_{MST} , (also referred to as the order-disorder transition).³⁴⁻³⁶ At room temperature, poly(ester-siloxane)s consist of a crystalline PBT-phase which is dispersed in an amorphous PDMS-phase. However, as the temperature is increased above a certain critical value, the size of the PBT-crystallites begins to decrease and the ordered microdomain structure changes to a disordered homogeneous phase (isotropic melt) at T_{MST} . The microphase separation transition temperatures for the poly(ester-siloxane)s were determined from Han's diagrams (plots of $\log G'$ versus $\log G''$, Fig. 8). The Han's diagrams show that microstructure transformations were

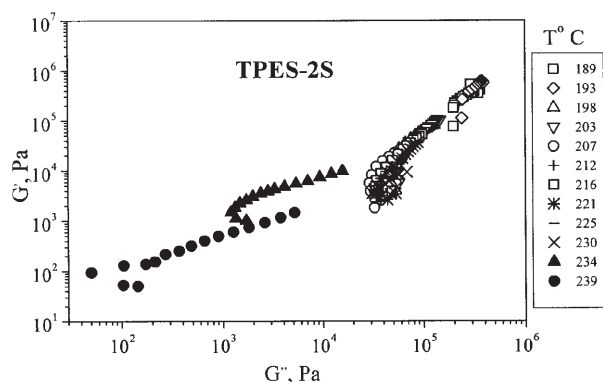


Fig. 8. $\log G'$ versus $\log G''$ for TPES-2S at different temperatures (Han's diagram).

manifested by changes in the shape and slope of the curves G' vs. 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 other words, T_{MST} is the lowest temperature at which the polymer melt is isotropic. The microphase separation transition temperatures for the investigated poly(ester-siloxane)s were in the range from 232 to 236 °C (Table V). The T_{MST} values were very similar, which was to be expected, as the structure and composition of the synthesized TPESs were similar.

CONCLUSIONS

Two series of thermoplastic poly(ester-siloxane)s were synthesized by catalyzed two-step transesterification–polycondensation reaction in the melt and in solutions of 1,2,4-trichlorobenzene. The reactants were dimethyl terephthalate, 1,4-butanediol and silanol-terminated poly(dimethylsiloxane) ($\bar{M}_n = 1750$ g/mol). In both series, the compositions of the reaction mixtures were varied in order to obtain a mass ratio of 55/45 for PBT/PDMS segments in the resulting copolymers. The synthesized poly(ester-siloxanes) had multiblock structures, as was confirmed by NMR analysis. The mass fraction of PBT segments lay between 55 to 65 % and the average lengths of the PBT segments lay between 11 and 16, calculated on 1 mole of soft segment, depending on the mole ratio of the reactants for the first series and on the amount of added solvent for the second one. It was concluded that the optimal BD/DMT ratio is 1.4, in which case, the obtained copolymer had an inherent viscosity of 0.54 dl/g. Investigation of the influence of the amount of 1,2,4-trichlorobenzene on the inherent viscosity showed that the inherent viscosity of the synthesized TPESs increases with increasing amount of added solvent. The optimal amount of the solvent in the reaction mixture was 50 mass %, in which case the obtained copolymer had the highest inherent viscosity. Extraction with chloroform showed that both the soluble and insoluble fractions had multiblock structures, while the homogeneity of the synthesized samples was not significantly improved in spite of the addition of solvent. The melting temperature of the TPESs was 223–224 °C, the enthalpy of melting 22.4–25.1 J/g and the degree of crystallinity,

calculated from the DSC data, was in the range from 15.5 to 17.4 %. The rheological measurements of poly(ester-siloxane)s performed in the dynamic mode showed that a microphase reorganization occurred during the melting process. The microphase separation transition temperatures, determined from Han's diagrams (plots of $\log G'$ versus $\log G''$) were in range from 232 to 236 °C. In the isotropic molten state, the dynamic complex viscosity increased with increasing content of PBT segments, as well as with their length.

ИЗВОД

СИНТЕЗА ТЕРМОПЛАСТИЧНИХ ПОЛИ(ЕСТАР-СИЛОКСАНА) У РАСТОПУ И РАСТВОРУ

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Две серије термопластичних еластомера на бази поли(диметилсилоксана) као меког сегмента и поли(бутилентерефталата) као тврдог сегмента синтетисане су катализованом трансестерификацијом полазећи од диметилтерефталата, DMT, силанол-терминарног поли(диметил-силоксана), PDMS-OH, $M_n = 1750$ g/mol и 1,4-бутандиола, BD. Молски однос почетних комомера одабран је тако да је резултовао у константном масеном односу тврдих и меких сегмената од 55:45. Прва серија је синтетисана са циљем да се одреди оптималан молски однос комомера BD и DMT за добијање термопластичних еластомера великих моларних маса. У другој серији синтезе су извођене у присуству тешко испарљивог растврача 1,2,4-трихлорбензена са циљем да се повећа мешљивост изузетно неполарног поли(диметилсилоксанског) претполимера и поларних реактаната, као што су DMT и BD и самим тим да се избегне фазна сепарација у реакционој смеси током синтезе. Структура и састав синтетисаних поли(естар-силоксана) потврђени су ¹H-NMR спектроскопијом, док су температура топљења и степен кристаличности одређени диференцијалном скенирајућом калометријом (DSC). Ефикасност уградње силанол-терминираниог поли(диметилсилоксана) у полиестарске ланце утврђена је на основу екстракције хлороформом. Реолошка својства поли(естар-силоксана) испитана су динамичко-механичком спектроскопијом.

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