

Application of reactive siloxane prepolymers for the synthesis of thermoplastic poly(ester–siloxane)s and poly(ester–ether–siloxane)s

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Abstract: Thermoplastic poly(ester–siloxane)s (TPES) and poly(ester–ether–siloxane)s, (TPEES), based on poly(butylene terephthalate) (PBT) as the hard segment and different siloxane-prepolymers as the soft segments, were prepared. The TPES and TPEES were synthesized by catalyzed two-step transesterification from dimethyl terephthalate, (DMT), 1,4-butanediol, (BD) and a siloxane-prepolymer. Incorporation of dicarboxypropyl- or disilanol-terminated poly(dimethylsiloxane)s (PDMS) into the polar poly(butylene terephthalate) chains resulted in rather inhomogeneous TPES copolymers, which was a consequence of a pronounced phase separation of the polar and non-polar reactants during synthesis. Two concepts were employed to avoid or reduce phase separation: 1) the use of siloxane-containing triblock prepolymers with hydrophilic terminal blocks, such as ethylene oxide (EO), poly(propylene oxide) (PPO) or poly(caprolactone) (PLC) when the terminal blocks serve as a compatibilizer between the extremely non-polar PDMS and the polar DMT and BD, and 2) the use of a high-boiling solvent (1,2,4-trichlorobenzene) during the first phase of the reaction. Homogeneity was significantly improved in the case of copolymers based on PCL–PDMS–PCL.

Keywords: thermoplastic elastomers, poly(ester–siloxane)s, poly(ester–ether–siloxane)s, phase separation, compatibility.

INTRODUCTION

Block copolymers as thermoplastic elastomers

Thermoplastic elastomers represent polymeric materials which show properties characteristic of chemically cross-linked elastomers, while possessing the processibility of thermoplastic materials. Combined thermoplastic and elastomeric behavior is characteristic for block copolymers, as well as for mixtures of elasto-

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mers and thermoplasts. Such a behavior is a consequence of the incompatibility of the segments of a copolymer or different polymers in a mixture. Incompatibility leads to phase segregation and the formation of a two-phase microstructure, *i.e.*, such a material is self-reinforced. Block copolymers which show thermoplastic and elastic behavior are composed of two types of blocks: soft, flexible blocks with a low glass transition temperature and hard, glassy or crystalline blocks, which provide physical crosslinking. Due to the two-phase microstructure, thermoplastic elastomers possess excellent mechanical properties, such as low-temperature flexibility, impact strength, toughness and high modules in the rubbery plateau region. At elevated temperatures, the physical bonds dissociate, allowing the copolymer to soften and flow like a thermoplastic material, enabling it to be processed in the melt by techniques such as injection molding.^{1,2}

Block copolymers with soft poly(siloxane) segments

Organic–siloxane block copolymers, due to the presence of poly(siloxane) chains, show lower glass transition temperatures, higher thermal and thermo-oxidative stability, as well as higher resistance to UV-radiation, atomic oxygen and ozone, enhanced permeability to many gases, hydrophobicity, biocompatibility and resistance to many solvents in comparison with common organic polymers. As a result of the mentioned properties, organic–siloxane copolymers have received special attention as elastomers, protective coatings, photoresists, biomaterials, gas separation membranes, emulsifiers, *etc.*³

Poly(dimethylsiloxane) has one of the lowest glass transition temperatures ($T_g = -123\text{ }^\circ\text{C}$) and a large molar volume ($75.5\text{ cm}^3/\text{mol}$). The chain flexibility and low intermolecular forces are also responsible for its low surface tension, low solubility parameters and low dielectric constant. Moreover, these properties show only a very small variation over a wide temperature range, which is also an important characteristic of poly(siloxane)s.^{3,4}

Reactive, telechelic siloxane oligomers are the most important starting material for the synthesis of siloxane-containing copolymers with properties of thermoplastic elastomers. Step-growth polymerization is usually used for the synthesis of such organo–siloxane copolymers, mainly due to the availability of a wide variety of well-defined, organofunctionally terminated, reactive siloxane oligomers (α,ω -telechelic siloxanes). The structures of α,ω -telechelic siloxane oligomers are presented in Fig. 1.

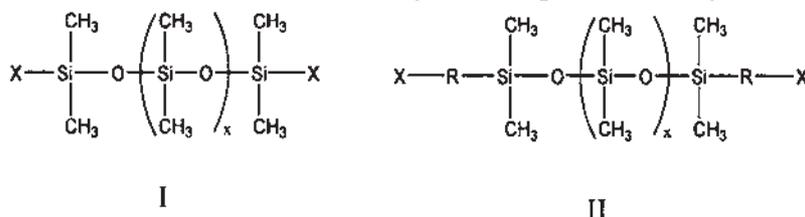


Fig. 1. Structure of α,ω -telechelic poly(dimethylsiloxane)s.

The main factors determining the reactivity of telechelic siloxane oligomers toward other reactants are the type and nature of the terminal functional groups. Due to the fundamental differences in their structures, chemical reactivities and overall properties, it is possible to divide functionally terminated siloxane oligomers into two groups. The first group (I in Fig. 1) consists of oligomers with Si-X terminal units and the other (II in Fig. 1) with Si-R-X units, where X and R represent the reactive functional group and a short organic moiety, respectively.

In most of the published reports about siloxane containing copolymers, the soft segment is almost exclusively poly(dimethylsiloxane). The extremely non-polar nature of PDMS, together with very low levels of inter and intramolecular attractions, leads to the formation of thermodynamically and mechanically incompatible blends with virtually all other polymers. This is reflected by the very low value of the solubility parameters of PDMS [$\delta = 15 \text{ (J/cm}^3)^{1/2}$],^{3,5} when compared with other polymers [$\delta = 15.4\text{--}28.0 \text{ (J/cm}^3)^{1/2}$].⁶ This is the most important driving force in the formation of two-phase microstructures in PDMS containing copolymers. Another very important factor which makes the morphology and structure-property relationships of siloxane copolymers somewhat unusual when compared with conventional organic block copolymers is the fact that at room temperature (20–25 °C), at which most of polymer experiments are conducted, PDMS is about 150 °C above its glass transition temperature. At these temperatures, due to the absence of inter and intramolecular interactions, PDMS segments should behave like a non-polar viscous liquid, thus providing perfect conditions for the formation of phase separated copolymer structures. In many cases, a siloxane molar mass as low as 500–600 g/mol (6–8 siloxane repeat units) and an organic segment having only a single repeat unit is sufficient to obtain two-phase morphologies.³ 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.^{7–12}

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 poly(butylene terephthalate) (PBT) as the hard segment, and different siloxane-prepolymers as the soft segments. TPES and TPEES were synthesized by catalyzed two-step transesterification, from dimethyl terephthalate, (DMT), 1,4-butanediol, (BD) and different siloxane-prepolymers. Incorporation of dicarboxypropyl- or disilanol-terminated poly(dimethylsiloxane) homopolymers (PDMS) into the polar poly(butylene terephthalate) chains resulted in rather inhomogeneous TPES copolymers, because of the pronounced phase separation of the polar and non-polar reactants during synthesis.^{13–16} All the prepared samples were partially soluble in chloroform, as a consequence of their significant structural and compositional inhomogeneity. Siloxane-containing triblock prepolymers with hydrophilic terminal blocks (which serve as a compatibilizer between

the extremely non-polar PDMS and the polar DMT and BD), such as ethylene oxide (EO), poly(propylene oxide) (PPO) or poly(caprolactone) (PCL),^{17,18} were used in further investigations to avoid phase separation during copolymer synthesis. Application of the high-boiling solvent (1,2,4-trichlorobenzene) during the transesterification step was also investigated in order to increase the miscibility of the polar and non-polar reactants.¹⁷

EXPERIMENTAL

Reactive siloxane prepolymers

α,ω -Dicarboxypropyl-poly(dimethylsiloxane)s (PDMS-CP, $\bar{M}_n = 550\text{--}2170$ g/mol) were prepared as described previously.¹⁹ α,ω -Disilanol-poly(dimethylsiloxane) (PDMS-OH, $\bar{M}_n = 2400$ g/mol), α,ω -dihydroxy-poly(ethylene oxide–dimethylsiloxane–ethylene oxide) (EO–PDMS–EO), α,ω -dihydroxy-poly(propylene oxide–dimethylsiloxane–propylene oxide) (PPO–PDMS–PPO), and α,ω -dihydroxy-poly(caprolactone–dimethylsiloxane–caprolactone) (PCL–PDMS–PCL) were supplied from ABCR (Germany). The number-average molar masses of the EO–PDMS–EO, PPO–PDMS–PPO and PCL–PDMS–PCL, were determined by ¹H-NMR spectroscopy; The \bar{M}_n of the prepolymer EO–PDMS–EO was 1100 g/mol, and the terminal ethylene oxide (EO) consisted of one unit. The number-average molar mass of the PPO–PDMS–PPO was 2900 g/mol, while the molar mass of the central poly(dimethylsiloxane) (PDMS) block was $\bar{M}_{\text{PDMS}} = 1100$ g/mol and molar mass of the terminal poly(propylene oxide) (PPO) blocks was $\bar{M}_{\text{PPO}} = 900$ g/mol. The \bar{M}_n of the PCL–PDMS–PCL was 6100 g/mol, with the molar mass of the central poly(dimethylsiloxane) (PDMS) block of $\bar{M}_{\text{PDMS}} = 2000$ g/mol. The molar mass of the terminal poly(caprolactone) (PCL) blocks was $\bar{M}_{\text{PCL}} = 2050$ g/mol.

Poly(ester–siloxane) and poly(ester–ether–siloxane) synthesis

Poly(ester–siloxane)s, TPES, and poly(ester–ether–siloxane)s, TPEES, were synthesized by catalyzed two-step reactions involving transesterification and polycondensation in the melt, under the optimal conditions, as was described in previous papers.^{13–17} The reactants were dimethyl terephthalate (DMT), 1,4-butanediol (BD), and the corresponding siloxane prepolymer (PDMS–CP, PDMS–OH, EO–PDMS–EO, PPO–PDMS–PPO or PCL–PDMS–PCL). The catalyst was tetra-*n*-butyl-titanate (1.0–2.5 mmol/mol DMT), while the thermal stabilizer was *N,N'*-diphenyl-*p*-phenylenediamine. The first step, transesterification, was carried out from 160 to 230–240 °C, at atmospheric pressure, when the formed methanol was distilled off. The second step, polycondensation, was performed for 1.5 to 4.5 h (depending on which prepolymer was used) at 230–250 °C, under reduced pressure. In this manner, several series of TPESs and TPEESs, with different soft segments and hard-to-soft weight ratios in the range from 90/10 to 40/60, were obtained. The synthesized TPES and TPEES samples were extracted with chloroform,^{13–17} and the obtained soluble and insoluble fractions were analyzed by ¹H-NMR spectroscopy.

A sample of a thermoplastic poly(ester–ether–siloxane) based on PPO–PDMS–PPO, was synthesized in solution (50 mass % of 1,2,4-trichlorobenzene in the reaction mixture).¹⁷

Characterization of the copolymers

¹H-NMR (200 MHz) spectra were obtained on a Varian Gemini-200 instrument. The TPES samples based on dicarboxypropyl- and disilanol-terminated poly(dimethylsiloxane)s, as well as the TPEES samples, were measured as solutions in CF₃COOD. The solvent was simultaneously used as the internal standard. The TPES samples based on PCL–PDMS–PCL prepolymers were measured as solutions in CDCl₃.

The inherent viscosities (η_{inh}) of the TPES and TPEES samples were measured in a mixture of phenol/trichloroethylene/toluene (1:1:2 by vol.) at 30 °C, using an Ubbelohde viscometer.

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC2 thermal analyzer. The DSC scans were recorded under a dynamic nitrogen atmosphere (flow rate 25 cm³/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. The samples were analyzed between 50 and 250 °C for the determination of the melting temperature (T_m) and the crystallization temperature (T_c) of the hard segment.

RESULTS AND DISCUSSION

Our work on siloxane containing copolymers started with the optimization of the synthesis of thermoplastic poly(ester-siloxane)s, TPESs, based on PBT as the hard segment and PDMS as the soft segment.¹³ The PDMS prepolymers used in the investigations differed in the reactive terminal groups (*i.e.*, either silanol- or carboxypropyl, Fig. 2). Poly(butylene terephthalate) was chosen as the hard segment in the thermoplastic elastomers because it has high structural regularity, crys-

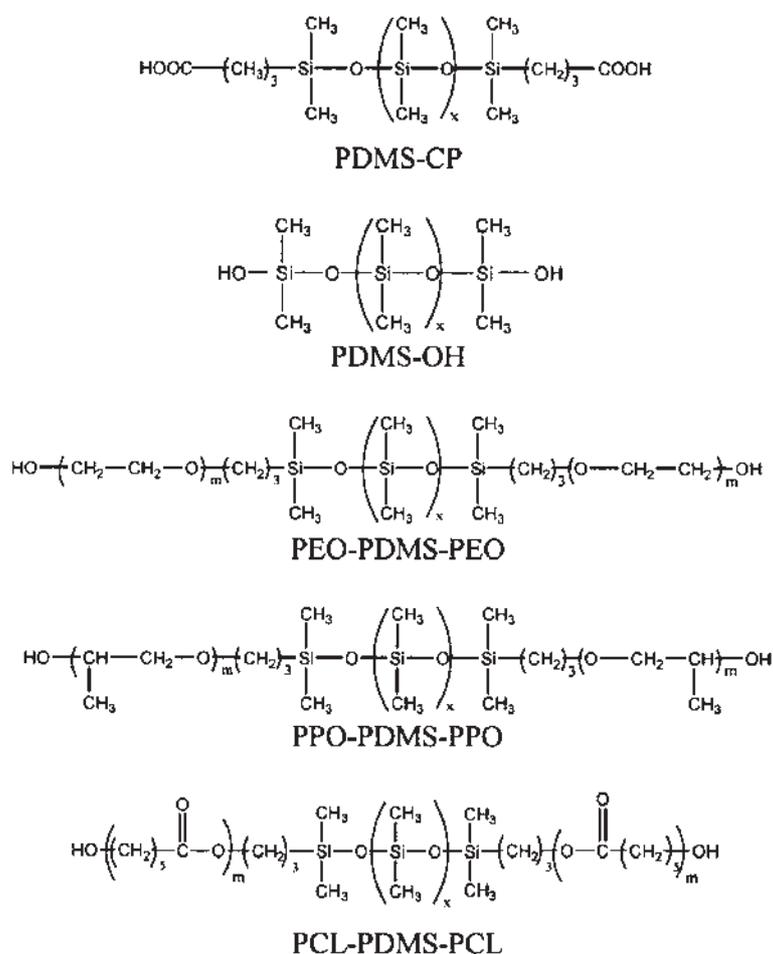


Fig. 2. Molecular structure of the prepolymers which were used as the soft segments for the preparation of thermoplastic poly(ester-siloxane)s and poly(ester-ether-siloxane)s.

tallizes rapidly and has a high degree of crystallinity.^{20,21} After the optimal reaction conditions had been established, the effect of the length of carboxypropyl-terminated PDMS prepolymers (550–2170 g/mol) on some characteristic properties of the TPES was examined, while the mass ratio of the hard and soft segments was kept constant (57/43).¹⁴ Further investigations were related to the effect of the mass ratio of the hard and soft segments on some properties of TPESs, with a constant length of the carboxypropyl-terminated PDMS prepolymer (1030 g/mol).¹⁵ Due to the high incompatibility of the extremely non-polar PDMS–OH and PDMS–CP with the polar reactants, DMT and BD, phase separation occurred during the reaction in the melt. It was observed that the PDMS prepolymers floated to the surface of the reaction mixtures when stirring was stopped during the transesterification step, hence the reaction mixture were not homogeneous. As a consequence, the incorporation of dicarboxypropyl- or disilanol-terminated PDMS into the polar poly(butylene terephthalate) chains resulted in rather inhomogeneous TPES copolymers.

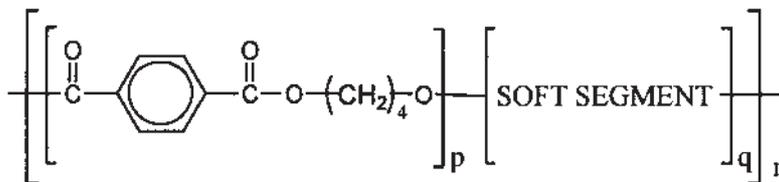


Fig. 3. Structure of the synthesized copolymers with hard PBT segments and soft segments based on siloxane prepolymers.

The effectiveness of the incorporation of PDMS prepolymers into the copolymer chains was proven by Soxhlet extraction with chloroform. It is well known that PBT-homopolymer is insoluble, while the PDMS-prepolymers are soluble in chloroform. The obtained results showed that all the examined samples were comprised of a soluble, as well as of an insoluble fraction (Table I). The TPES samples based on PDMS–CP prepolymer lost 19–42 mass % during extraction. The composition and structure of the soluble and insoluble fractions were investigated by ¹H-NMR spectroscopy. The spectra of both fractions contained signals of aromatic rings from the PBT segments and also signals of Si–CH₃ protons from the PDMS segments. The spectra also showed that the extracted and insoluble fractions differed in both their composition and structure, containing considerably different amounts of PDMS and PBT segments (Table I). The soluble fractions of the TPES samples contained 66–89 mass % of PDMS segments, while the insoluble fractions contained only 13–58 mass %. The calculated value of *p* (the average degree of butylene terephthalate units in the hard segments, Fig. 3) in the soluble fractions was very small ($p_{\text{sol}} = 1.0\text{--}2.9$), while in the insoluble fractions, it was much higher ($p_{\text{ins}} = 3.5\text{--}32.1$). It can be concluded that both the extracted and insoluble fractions have a segmented (multiblock) structure, but with shorter PBT blocks in the soluble and longer ones in the insoluble fractions. As the used PDMS–CP polymer was polydisperse, it was not unexpected that longer PDMS chains (1130–1640

g/mol) were found in the soluble, and shorter chains (610–990 g/mol) in the insoluble TPES fractions, as show by $^1\text{H-NMR}$ spectroscopy.

In order to avoid or reduce phase separation during the synthesis of PDMS containing thermoplastic elastomers, two concepts were employed in further investigations: a) hydroxy-terminated triblock (ABA) prepolymers with hydrophilic terminal blocks, *i.e.*, ethylene oxide (EO), poly(propylene oxide) (PPO) or poly(caprolactone) (PCL) and with a central PDMS block (Fig. 2) were used and b) a high-boiling solvent was used during the first phase of the reaction. It was expected that the terminal EO, PPO or PCL blocks would serve as a compatibilizer between the extremely non-polar PDMS and the polar DMT and BD.

It was shown that the presence of ether chains, either EO or PPO in the siloxane containing prepolymers 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 and PDMS–OH prepolymers. The compositions of the chloroform soluble and insoluble fractions of the TPEES samples are also presented in Table I.

TABLE I. Inherent viscosities (η_{inh}) and $^1\text{H-NMR}$ analysis of the chloroform soluble and insoluble fractions of some of the TPES and TPEES samples

Sample	PBT/soft segment mass %	η_{inh} dl/g	Soluble/Insoluble founded %	Soluble fractions		Insoluble fractions	
				mass % of soft segments	p_{sol} in Fig. 3	mass % of soft segments	p_{ins} in Fig. 3
TPES based on PDMS–CP prepolymer, $\overline{M}_{n\text{PDMS-CP}} = 1030$ g/mol							
TPES1	70/30	0.37	19/81	83	1.2	13	32.1
TPES2	60/40	0.43	25/75	79	1.7	18	21.9
TPES3	55/45	0.45	42/58	66	2.9	17	23.4
TPES4	50/50	0.44	39/61	89	1.0	31	10.7
TPES5	40/60	0.35	41/59	86	1.0	58	3.5
TPEES based on EO–PDMS–EO prepolymer, $\overline{M}_{n\text{EO-PDMS-EO}} = 1100$ g/mol							
TPEES-A1	90/10	0.38	3/97	82	1.2	4	134.1
TPEES-A2	80/20	0.38	13/87	82	1.2	7	77.7
TPEES-A3	70/30	0.43	26/74	81	1.3	10	52.5
TPEES-A4	60/40	0.61	26/74	86	1.0	16	29.8
TPEES-A5	50/50	0.76	34/66	83	1.2	24	18.1
TPEES-A6	40/60	0.47	56/44	82	1.2	19	24.0
TPEES based on PPO–PDMS–PPO prepolymer, $\overline{M}_{n\text{PPO-PDMS-PPO}} = 2930$ g/mol							
TPEES-B1	60/40	0.48	39/61	88	2.0	19	61.5
TPEES-B2	55/45	0.44	43/57	88	1.8	19	61.5
TPEES-B3	50/50	0.44	39/61	89	1.7	25	41.0
TPEES-B1S ^{a)}	60/40	0.52	36/64	86	2.2	19	61.5

^{a)} Synthesis performed in solution using 1,2,4-trichlorobenzene as solvent

The TPEES samples based on the EO–PDMS–EO prepolymer lost 3–56 mass % during extraction. The sample TPEES-A4 lost 26 mass % during extraction, similar to the TPES2 sample based on the prepolymer PDMS–CP (25 mass %). The samples TPES2 and TPEES-A4 had the same PBT/(soft segment) ratio (60/40) and almost the same length of the soft segment ($\bar{M}_{n\text{PDMS-CP}} = 1030$ g/mol and $\bar{M}_{n\text{EO-PDMS-EO}} = 1100$ g/mol). The soluble fraction of the TPEES-A4 sample contained 86 mass % of soft segments (EO–PDMS–EO), while the insoluble fraction contained 16 mass %. The soluble and insoluble fractions of the sample TPES2 contained 79 and 18 mass % of soft, PDMS segments, respectively. It can be concluded that the length of the EO block (only 1 repeating unit) was too short to be an efficient compatibilizer between PBT and PDMS, in spite of its high solubility parameter [$\delta_{\text{PEO}} = 20.2$ (J/cm³)^{1/2}],⁵ which is close to the solubility parameter of PBT [$\delta_{\text{PBT}} = 23.0$ (J/cm³)^{1/2}].⁶

The TPEES samples based on the PPO–PDMS–PPO prepolymer lost 36–43 mass % during extraction. The sample TPEES-B1, with a PBT/(soft segment) ratio of 60/49, lost 39 mass % during extraction, which indicates a relationship between the soft segment length and the amount of soluble fraction. The samples TPES2 and TPEES-A4, with the same hard/soft segment ratio, but with shorter soft segments, lost 25 and 26 mass %, respectively. The soluble fractions of the PPO–PDMS–PPO based TPEES contained 86–89 mass % of soft segments, while the insoluble fractions contained 19–25 mas %. In the case of the PPO–PDMS–PPO based TPEES, it can be concluded that the compatibilizing effect between PBT and PDMS was not realized, because of the rather low solubility parameter of PPO [$\delta_{\text{PPO}} = 15.4$ (J/cm³)^{1/2}],^{6,22} which is very close to the solubility parameter of PDMS [$\delta_{\text{PDMS}} = 15$ (J/cm³)^{1/2}].³

The calculated value of p in the TPEES soluble fractions was very small ($p_{\text{sol}} = 1.0$ – 2.2) and similar to the p_{sol} values of the TPES samples. In the insoluble fractions, it was much higher for the PPO–PMDS–PPO based TPEES ($p_{\text{ins}} = 61.5$ for TPEES-B1) than for the EO–PDMS–EO based TPEES ($p_{\text{ins}} = 29.8$ for TPEES-A4) at the same PBT/(soft segment) ratio (60/40). The length of the PBT segments in the insoluble fraction is directly related to the molar mass of the prepolymer which was used for the copolymer synthesis, at a fixed mass ratio of hard-to-soft segments (Table I).

With the intention of improving the miscibility of the reaction mixture and, therefore, the effectiveness of the incorporation of the PPO–PDMS–PPO prepolymer into the PBT chains, the sample TPEES-B1S was prepared in solution using the high boiling solvent 1,2,4-trichlorobenzene. A clear solution was obtained at the synthesis temperature. The transesterification reaction in solution was more efficient than in the melt.¹⁷ It was shown that the efficiency of transesterification has an effect on the further course of the copolymer synthesis, *i.e.*, on the polycondensation, and, finally, on the molar mass of the obtained copolymer. The inherent viscosity (which is an indicator of molar mass) of TPEES-B1S ($\eta_{\text{inh}} = 0.52$ dl/g), was higher than that of TPEES-B1 ($\eta_{\text{inh}} = 0.48$ dl/g), which had the same composition

but was synthesized in the melt. Extraction with chloroform showed that both the soluble and insoluble fractions had multiblock structures, although the homogeneity of TPEES-B1S was not improved over that of TPEES-B1 in spite of the addition of solvent (Table I).

The series of TPES copolymers based on PBT and poly(caprolactone)-poly(dimethylsiloxane)-poly(caprolactone) with hard-to-soft segment ratios in the range from 80/20 to 40/60 were completely soluble in chloroform, which enabled their molar masses to be determined by gel-permeation chromatography (GPC). The chromatograms showed the presence of only one peak, the shape of which corresponded to a typical high-molecular weight product of step-growth polymerization. It is obvious that the presence of the longer (18 repeating units), polar poly(caprolactone) blocks [$\delta_{\text{PCL}} = 20.0 \text{ (J/cm}^3)^{1/2}$],^{23,24} played a significant role in the improvement of the miscibility of the prepolymer with the polar reactants and PBT. The reaction mixture was homogeneous, as were the synthesized copolymers with respect to their structure and composition.

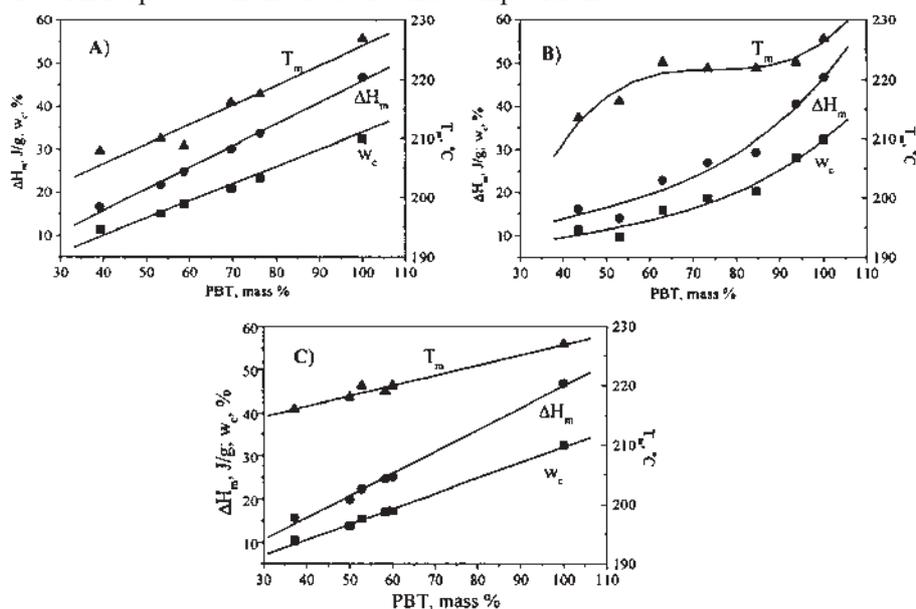


Fig. 4. Change in the melting temperature (T_m), enthalpy of melting (ΔH_m) and degree of crystallinity (w_c), measured by DSC, with changing mass fraction of PBT segments for the poly(ester-siloxane) series with soft segments based on PDMS-CP prepolymer (A) and the poly(ester-ether-siloxane) series with soft segments based on EO-PDMS-EO prepolymer (B) or PPO-PDMS-PPO prepolymer (C).

The synthesized TPES and TPEES were semi-crystalline copolymers. The melting temperatures (T_m) of the hard segments were observed by DSC. The DSC measurements were performed between 50 and 250 °C to determine T_m , the enthalpy of melting (ΔH_m) and the degree of crystallinity (w_c) of the TPES and

TPEES samples, and for the sake of comparison, of PBT-homopolymer. With increasing mass fraction of PBT segments, the melting temperature shifted gradually to higher values, from 208 to 218 °C for TPES samples based on PDMS segments, from 214 to 223 °C for TPEES samples based on EO–PDMS–EO segments and from 216 to 220 °C for TPEES samples based on PPO–PDMS–PPO segments (Fig. 4). The melting temperature of the PBT-homopolymer was 227 °C. The enthalpies of melting were calculated from the corresponding thermograms. The total degree of crystallinity, *i.e.*, the mass fraction of crystallinities in the TPES and TPEES copolymers, were calculated from the determined ΔH_m using the equation:

$$w_c = \Delta H_m / \Delta H_m^\theta$$

where $\Delta H_m^\theta = 144.5$ J/g is the enthalpy of melting of perfectly crystalline PBT-homopolymer.⁶

The melting temperature, the enthalpy of melting and the degree of crystallinity of the TPES and TPEES increased with increasing mass fraction of the hard PBT segments, as presented in Fig. 4.

CONCLUSIONS

Thermoplastic elastomers with hard segments based on poly(butylene terephthalate) (PBT) and soft segment based on: a) poly(dimethylsiloxane) (PDMS) or b) prepolymers with central PDMS blocks and terminal ethylene oxide (EO), poly(propylene oxide) (PPO) or poly(caprolactone) (PCL) block were synthesized by two-step transesterification in the melt. The poly(ester–siloxane)s based on PDMS segments and the poly(ester–ether–siloxane)s based on EO–PDMS–EO or PPO–PDMS–PPO segments were rather inhomogeneous. After extraction with chloroform, soluble and insoluble fractions of different structure and composition were obtained. In the presence of a high-boiling solvent (1,2,4-trichlorobenzene), the molar mass of the synthesized poly(ester–ether–siloxane) based on PPO–PDMS–PPO showed a modest increase. Extraction with chloroform showed that both the soluble and insoluble fractions had multiblock structures, but the homogeneity of the sample was not significantly improved by the addition of the solvent. Due to the presence of long, polar PCL blocks, the miscibility of the PCL–PDMS–PCL prepolymer with the polar monomers in the reaction mixture was significantly improved, in comparison with all the other examined systems. As a result, the obtained PCL–PDMS–PCL based copolymers were structurally and compositionally homogeneous and completely soluble in chloroform. The semi-crystalline structure of the poly(ester–siloxane)s and poly(ester–ether–siloxane)s was confirmed by DSC analysis. With increasing mass fraction of hard-PBT segments, the melting temperature, the enthalpy of melting and the degree of crystallinity of the TPES and TPEES increased.

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ИЗВОД

ПРИМЕНА РЕАКТИВНИХ СИЛОКСАНСКИХ ПРЕТПОЛИМЕРА ЗА
СИНТЕЗУ ПОЛИ(ЕСТЕР–СИЛОКСАНА) И
ПОЛИ(ЕСТЕР–ЕТАР–СИЛОКСАНА)

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У оквиру овог рада су синтетисани термопластични поли(естар–силоксани) (TPES) и поли(естар–етар–силоксани) (TPEES), са тврдим сегментима на бази поли(бутилентерефталата) (PBT) и меким сегментима на бази различитих силоксанских претполимера. TPES и TPEES су синтетисани катализованом реакцијом двостепене трансестерификације, из диметилтерфталата (DMT), 1,4-бутандиола (BD) и одговарајућег силоксанског претполимера. При уградњи дикарбоксипропил- или дисиланол-терминираних поли(диметилсилоксана) (PDMS) у поларне поли(бутилентерефталатне) ланце добијени су прилично нехомогени TPES кополимери, што је била последица лоше мешљивости реактаната током одигравања реакције. Примењена су два концепта да би се избегло или смањило фазно раздвајање реакционе смеше током синтезе органо–силоксанских кополимера: 1) примена силоксанских триблок-претполимера код којих су хидрофилни терминални блокови, изграђени од етиленоксида (EO), поли(пропиленоксида) (PPO) или поли(капролактона) (PLC), имали функцију компатибилизатора између неполарног PDMS-а и поларних реактаната, DMT-а и BD-а и 2) примена растварача високе температуре кључања (1,2,4-трихлорбензена) за време извођења прве фазе реакције. Значајно повећање хомогености постигнуто је код кополимера на бази PCL–PDMS–PCL сегмената.

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REFERENCES

1. G. Holden, "Elastomers thermoplastic", in *Encyclopedia of Polymer Science and Engineering*, Vol. 5, J. Wiley, New York, 1987, p. 416
2. H. Schroeder, R. J. Cella, Polyesters, elastomeric, in *Encyclopedia of Polymer Science and Engineering*, Vol. 12, Wiley, New York, 1987, p. 75
3. I. Yilgor, J. E. McGrath, *Adv. Polym. Sci.* **86** (1988) 1
3. P. R. Dvornic, R. W. Lenz, *High Temperature Siloxane Elastomers*, Huthing & Wepf, Heidelberg, New York, 1990
5. E. A. Grulke, in *Polymer Handbook*, J. Brandrup, E. H. Immergut, Eds., New York, Wiley, 1989 p. 519
6. D. W. VAN Krevelen, *Properties of Polymer*, Elsevier, Amsterdam, 1990
7. P. R. Ginnings, US Patent, 4 496 704 (1985)
8. D. J. De Yong, G. J. Murph, US Patent 5 132 392 (1992)
9. T. Nakane, K. Hijakata, Y. Kageyama, K. Takahashi, US Patent 4 927 895 (1990)
10. R. L. Ostrozynski, G. H. Green, J. H. Merfified, US Patent 4 766 181 (1988)
11. N. Yamamoto, H. Mori, A. Nakata, M. Suehiro, US Patent 4 894 427 (1990)
12. R. Mikami, M. Yoshitake, T. Okawa, US Patent 5 082 916 (1992)
13. V. V. Antić, M. R. Balaban, J. Djonlagic, *Polym. Int.* **50** (2001) 1201
14. V. V. Antić, M. N. Govedarica, J. Djonlagic, *Polym. Int.* **52** (2002) 1188
15. V. V. Antić, M. N. Govedarica, J. Djonlagic, *Polym. Int.* **53** (2004) 1786
16. B. P. Dojčinović, V. V. Antić, M. V. Vučković, J. Djonlagic, *J. Serb. Chem. Soc.* **70** (2005) 1471
17. M. V. Vučković, V. V. Antić, B. P. Dojčinović, M. N. Govedarica, J. Djonlagic, *Polym. Int.* **55** (2006) 1304

18. S. Randjelović, V. V. Antić, B. P. Dojčinović, M. V. Vučković, M. N. Govedarica, J. Djonlagić, *Unpublished results*
19. V. M. Djinović, V. V. Antić, M. N. Govedarica, J. Djonlagić, *React. Funct. Polym.* **44** (2000) 299
20. C. F. Pratt, S. Y. Hobbs, *Polymer* **17** (1976) 12
21. M. Yokouchi, Y. Sakakibara, Y. Chatani, H. Tadokoro, T. Tanaka, K. Yoda, *Macromolecules* **2** (1976) 266
22. Aldrich Catalog Number Z41,247-3, Polymer solutions: Solvents and Solubility Parameters, Table IV
23. A. Sarac, A. Ture, O. Cankurtaran, F. Yilmaz, *Polym. Int.* **51** (2002) 1285
24. <http://www.caprolactones.com/oproducts/catalogue/>.