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Synthesis and Properties of Poly(butylene terephthalate)-Poly(ethylene oxide)-Poly(dimethylsiloxane) Block Copolymers

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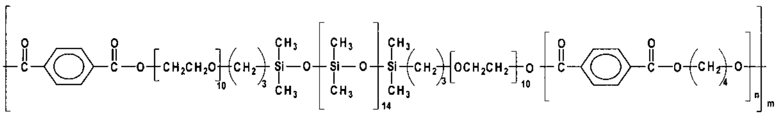
Summary:



Poly(butylene terephthalate)-poly(ethylene oxide)-poly(dimethyl siloxane)-poly(ethylene oxide) block copolymers, (PBT-PEO-PDMS-PEO)$_m$, are synthesized by polycondensation (PC) of dimethylterephtalate (DMT), 1,4-butanediol (BDO) and PEO-PDMS-PEO. The soft block has been incorporated from 10 to 70 wt-%; the total molecular weight (MW) of the block-copolymers amounts to 16000 – 20000 g/mol.
One major problem of polyether-PBT thermoplastic elastomers is their poor thermo-oxidative stability. Due to the excellent heat stability of PDMS, the resistance of this new thermoplastic elastomer against thermo-oxidative degradation has been increased 80 %!
From differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) in the PEO-PDMS-PEO based COPEs, three phases can be distinguished. Besides the crystalline PBT phase, an amorphous mixed phase of PBT and PEO and an almost pure PDMS phase have been found. Due to the high concentration of the mixed PBT-PEO phase, the low temperature modulus and the glass transition temperature, T_g, are not dominated by the pure PDMS phase (T_g = -114 °C). Depending on the amount of PBT and PEO present, the main glass transition lies in the range of –50 °C to 50 °C.

Keywords: morphology, polycondensation, polysiloxanes, thermo-oxidative stability

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1 Introduction

COPEs are segmented co-polymers with an $[\text{-A-B-}]_m$ structure with A being a polyether and B an aromatic polyester segment. COPEs are semicrystalline polymers with a crystalline polyester hard phase and a mixed amorphous phase.[1] These thermoplastic elastomers combine the elasticity and flexibility of rubbers and the easy processability of thermoplastics. Thus, injection molding, extrusion and blow molding can be applied for processing the material. In contrast to rubbers, COPEs can be recycled. Due to their good mechanical properties at a broad range of temperatures, high abrasion and solvent resistance and tear fatigue, they are used in a broad spectrum of applications. The automotive industry is the main end user, COPE being applied in boots and bellows, air ducts, and airbag covers. COPE films are used in roofing and textile lamination. Furthermore, COPEs are used in electric and electronic applications, for example for cable insulation and connectors. Moreover, mechanical goods as belting, tubes and hoses and keypads are made from COPEs.[1]

Silicones possess an excellent high- and low temperature stability, UV resistance, very good low temperature flexibility due to their low $T_g \sim -123$ °C, high gas permeability and a low surface tension. Incorporating them into a polyester backbone would combine these advantages with the melt processability of a plastic. Ten years ago, first works about incorporation of PDMS (instead of polyether) chains into polyester backbones have been published.[2-8] R. Mikami and coworkers encountered difficulties to co-polymerize DMT, BDO and hydroxy-terminated polyalkylsiloxanes. A significant fraction of siloxane was not incorporated into the polyester backbone. They explained this by the lack of compatibility between the polar PBT and the apolar siloxane.[7] D. A. Schiraldi studied the synthesis and properties of PDMS-PBT block copolymers [8]. The author reported that for concentrations higher than 15 wt-%, a loss of mechanical properties has been observed, and at higher contents, the polymers showed a lack of cohesiveness due to the incompatibility between the PBT and PDMS phases. D. J. Young and co-workers claim polyether-polysiloxane-polyether triblock copolymers with alkyl and polyether substituents (Figure 1) to increase the hydrophilicity of the surface of fibers and films.[5] The hydrophilic ether substituents of the siloxane allow complete miscibility with the aromatic polyester and due to the OH termination also covalent incorporation into the polyester backbone.

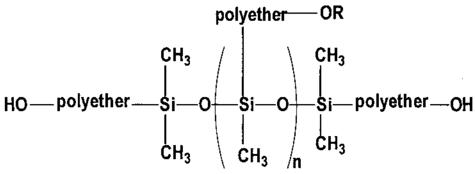


Fig. 1. Polyether-polysiloxane-polyether triblock copolymers with alkyl and polyether substituents.[5]

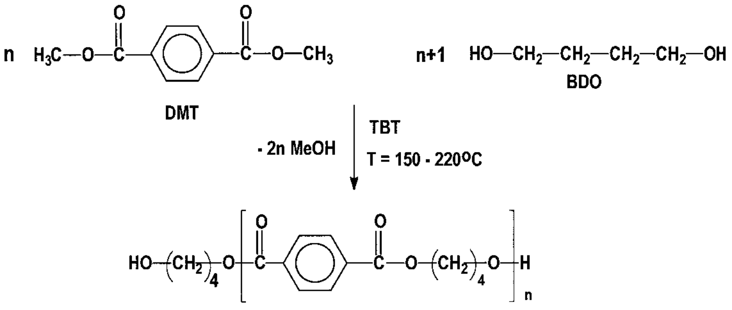
In this article, we describe the synthesis of PBT-PEO-PDMS-PEO block copolymers. The PEO serves as a compatiblizer between the hydrophobic PDMS and the hydrophilic PBT. Thus, the PEO-PDMS-PEO soft block is not completely miscible as the copolymer shown in Figure 1, but also not as immiscible as pure hydroxyl-terminated PDMS.

2 Results and Discussion

First, the preparation of $(PBT\text{-}PEO\text{-}PDMS\text{-}PEO)_m$ block copolymers is discussed. Then, the thermo-oxidative properties and morphology of these new COPEs are presented.

2.1 Synthesis of $(PBT\text{-}PEO\text{-}PDMS\text{-}PEO)_m$ Block Copolymers

The copolymers are synthesized in two reaction steps: First, the transesterification (TE) takes place between DMT and BDO to form PBT oligomers (Scheme 1) by gradually heating the mixture to 220°C. BDO is present with 40 mol-% excess. The DMT can also react with the OH end groups of the soft block and form a prepolymer. Then, during polycondensation (PC) the prepolymers react under evaporation of the excess BDO and the molecular weight (MW) increases (Scheme 2). The PC is carried out by gradually raising the temperature from 230 – 245 °C under high vacuum (< 1mbar). The TE and PC are catalyzed by tetrabutyl titanate (TBT) and magnesium acetate tetrahydrate, added at equimolar quantities. The catalyst and co-catalyst concentration amount to 1.128 mmol for 800 g polymer, assuming 100% conversion. 0.5 wt-% of the phenolic anti-oxidant Irganox 1330 are added to avoid oxidative degradation. Silicon oil is used as anti-foaming agent.



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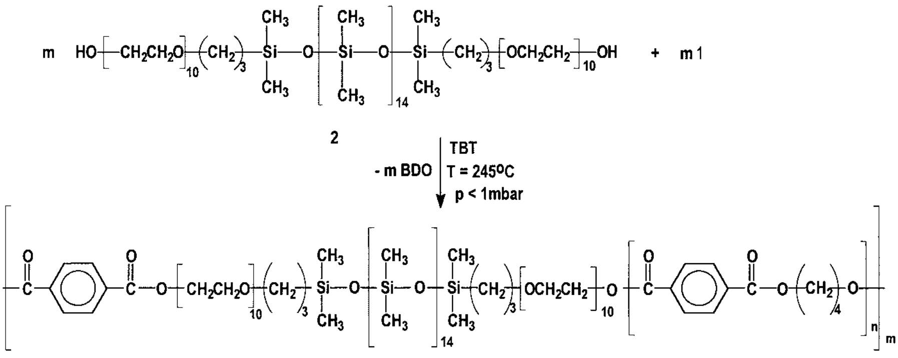
Scheme 1. Transesterification and formation of PBT-oligomers.



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Scheme 2. Polycondensation.

The polymerization reaction is stopped, when the target torque is reached. The concentration of the soft block **2** has been varied from 10 – 70 wt-% (Table 1).

Up to 60 wt-% of **2** (MW = 2200 g/mol), melt phasing occurred at T = 245 °C; for higher concentrations the melt was clear. A milky appearance of the melt means that the soft and hard segments are no longer compatible under the conditions of the PC. Generally, at the transition from the one phase regime to the two phase regime, the effects of melt phasing are small and the copolymers exhibit one T_g and one melting point (T_m). Deep in the two-phase regime, two liquid phases exit, one rich in soft block and the other rich in hard block. These polymer blends have then also two T_g and two T_m [9]. According to [10], the resulting polymers have low tensile and tear strength and have a short elongation at break.

Table 1. Content of **2**, appearance of the melt at 245 °C, PC-time and torque at the end of PC at 20 rpm of PBT-PEO-PDMS-PEO block copolymers.

Sample	**2** [wt-%]	Melt	PC-Time [min]	Torque at 20 rpm [Nm]
S1	10	Milky	36	2.1
S2	30	Milky	40	2.4
S3	45	Milky	45	2.3
S4	50	Milky	75	2.30
S5	55	Turbid	100	2.2
S6			164	4.0
S7	65	Clear	225	1.8
S8	70	Clear	195	0.6

The purity of **2** has been investigated with ^1H and ^{13}C NMR. In the ^1H spectrum, the main resonances can be located at 3.55 ppm (m) $OC\underline{H}_2$ PEO, 3.3 ppm (t) $OC\underline{H}_2$ PEO/PDMS transition, 1.5 ppm (m) $C\underline{H}_2$ PDMS, 0.5 ppm (m) CH_2 PDMS, 0 ppm (s) Si-$(C\underline{H}_3)_2$ PDMS. The R-O-CH_2-CH_2-OH end groups could not be assigned unambiguously in the ^1H spectrum, in the ^{13}C spectrum these resonances were easily identified by the –$C\underline{H}_2$-OH resonance at 61.0 ppm. These signals are of higher intensity then those of the PEO-PDMS transitions at 23.7 and 14.5 ppm, indicating the presence of free PEO. Assuming the same average chain length, the free PEO amounts up to 25 wt-% (30 mol-%). The calculated MW of the PEO block is 830 g/mol and of the PDMS block 1160 g/mol.

The ^1H spectrum also reveals several end group resonances at 6.1 ppm (dd), 5.9 ppm (dd), 4.7 ppm (dq) and 4.3 ppm (dq) that have been assigned to both cis and trans propenyl (vinylene) end groups CH_3-$C\underline{H}$=$C\underline{H}$-OR. Their amount is 15 and 12 % of the total number of RO-CH_2-CH_2-OH end groups. Mostly, PDMS is linked to PEO by hydrosilylation of PEO containing an OH and a vinyl end group [5]. As PEO is added in excess, PEO-PDMS-PEO block copolymers contain free PEO. Each free PEO chain is terminated on one end by a vinyl group. Therefore, the percentage of unsaturated end groups (27 %) and the mol-% free PEO, determined from the excess –$C\underline{H}_2$-OH resonance (30 mol %), correspond very well.

As the free PEO chains have only one OH end group, they act as chain stoppers during PC; thus, the PC-time increases with the soft block content.

The number average molecular weight (M_n) of all samples has been determined from the concentration of hydroxyl (E_{OH}), carboxyl (E_C) and unsaturated end groups (E_{UNS}), which are listed in Table 2.

Table 2. E_C, E_{OH}, E_{UN} and M_n of all $(PBT\text{-}PEO\text{-}PDMS\text{-}PEO)_m$ block-copolymers.

Sample	E_C [meq/kg]	E_{OH} [meq/kg]	E_{UNS}[a] [meq/kg]	M_n [g/mol]
S1	11	79	10	20000
S2	15	73	30	17000
S3	13	67	45	16000
S4	20	50	50	17000
S5	20	49	55	16000
S6	14	48	55	17000
S7	18	34	65	17000
S8	15	37	70	16000

[a] The unsaturations of **2** are known from ^1H NMR; E_{UNS} has been calculated assuming that no further unsaturations are formed during PC.

The most striking observation is that independent of the final torque at 20 rpm, M_n amounts to about 17000g/mol. Even S5 and S6, where there is 100 % difference in torque, the M_n are nearly identical. The torque is determined by the melt viscosity and thus the weight average molecular weight (M_w) for non entangled chains or the viscosity average molecular weight for entangled chains.[11] We hypothesize that due to the high E_{UNS} crosslinking occurs, effecting more M_W than M_n. This might explain, why for S5 and S6 a 100 % increase in torque leads only to 6 % increase in M_n.

The incorporation of **2** has also been verified with ^1H NMR. In these spectra, the main resonances can be found at 8.0 ppm (s) aromatic H PBT, 4.38 ppm (t) $OC\underline{H}_2$ PBT, 3.57 ppm (t) $OC\underline{H}_2$ PEO, 1.91 ppm (t) $C\underline{H}_2$ PBT and 0.05 ppm (s) $Si\text{-}(C\underline{H}_3)_2$ PDMS. At a lower level, the signals from PEO-PDMS transitions can be found at 4.44 ppm (t) $C(O)OC\underline{H}_2$, 3.78 ppm (t) $C(O)OCH_2\text{-}C\underline{H}_2\text{-}O$, 3.37 ppm (t) $OC\underline{H}_2$, 1.68 ppm $C\underline{H}_2$ PDMS and 1.50 ppm $\text{-}C\underline{H}_2Si$ PDMS. Based on these signals, the overall composition of the copolymers has been calculated (Table 3).

Table 3. Overall composition of PBT-PEO-PDMS-PEO block copolymers determined with ^{1}H NMR.

Sample	PBT	PBT	PEO	PEO	PDMS	PDMS
	wt-%	MW [g/mol]	wt-%	MW [g/mol]	wt-%	MW [g/mol]
S2	72	3500	13	780	15	1100
S6	46	1000	25	810	29	1000

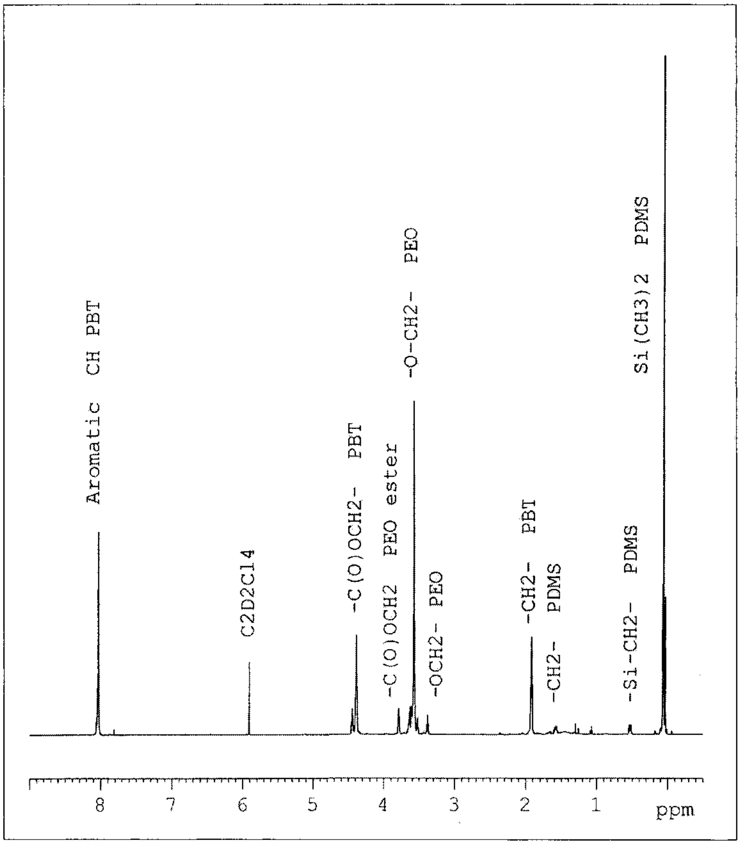

Fig. 2. ^{1}H NMR of S6.

With increasing PBT content, the MW of the PBT blocks increases. As expected, the MWs of the PEO and PDMS blocks do not change during polymerization. For PBT, the MW is calculated from the signals at 8.0 and 4.38 ppm. The MW of the PDMS block is determined from the

$Si(CH_3)_2$ signals at 0.05 ppm and the PEO-PDMS transitions at 0.50 and 1.5 ppm. In Figure 2, a typical ^1H NMR spectrum is shown.

2.2 Morphology

In Figure 3a, the atomic force microcopic (AFM) picture of sample S6 with 55 wt-% soft block is depicted. As a comparison, the picture of a PBT-polyether block-copolymer with 55 wt-% of a poly(ethylene oxide)/poly(propylene oxide) (PEO/PPO) copolyether is shown in Figure 3b. The AFM was operated in tapping mode, thus the contrast comes from the difference in hardness of the different phases. The hard crystalline PBT phase is represented by a light color, while the soft amorphous phase is dark. (The long light thin lines are arte facts of the preparation of the sample, which result from scratches on the teflon.) From Figure 3 it becomes obvious that the silicon based COPE shows less crystalline PBT than the corresponding COPE based on PEO/PPO soft blocks. Moreover, the crystalline PBT is co-continuous in case of the PBT-polyether block copolymer, while it is disperse in the silicon based COPE. Such a disperse morphology was also observed for PBT-polyether block-copolymer after stretching beyond their yield point.

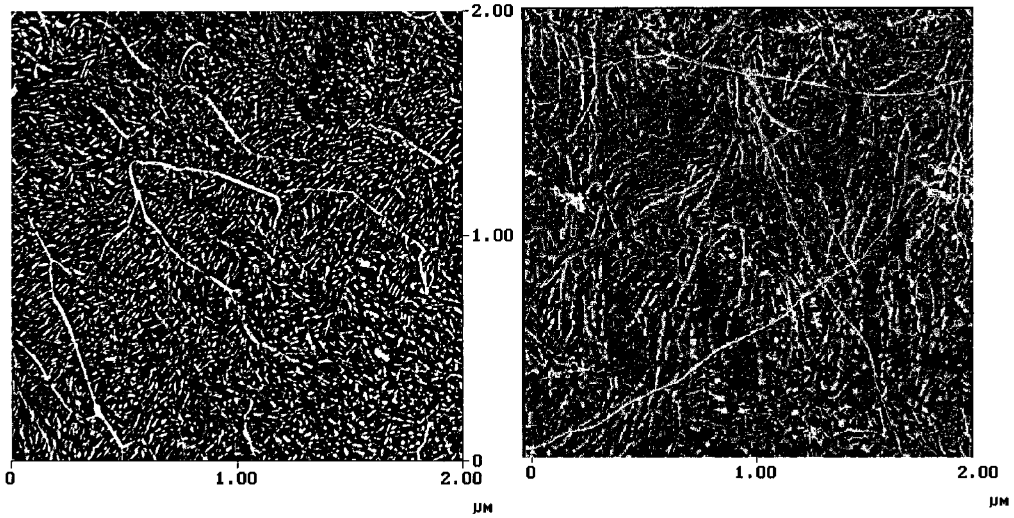

Fig. 3a/b. Tapping mode AFM on sample S6 with 55 wt-% PEO-PDMS-PEO soft block (left) and on a PBT-polyether blockcopolymer based on 55 wt-% PEO/PPO copolyether.

2.3 Thermal Analysis

In Table 4, the results of the DSC are listed. For all samples, a T_g at –114 °C has been observed. This T_g is close to that of pure PDMS (-123 °C), indicating that the PDMS is strongly phase separated. Although the appearance of the melt for the samples up to 55 wt-% soft block has been milky, all samples only show one melting peak. This is typical for not macro-phase separated COPEs. With increasing amount of soft block, T_m decreases from 217 °C to ca. 153 °C. This decrease can be explained by the decrease of the average degree of polymerization of the PBT blocks with increasing amount of soft block. For polyether based COPE, the T_ms of the PBT are strongly coupled to the average degree of polymerization of the PBT blocks and are independent of the type of ether soft block, as can be seen from Figure 4. However, the PDMS based materials seem to behave differently. Comparing polyether based COPEs and PEO-PDMS-PEO based COPEs with the same average degree of polymerization of the PBT, the silicon based materials show up to 40 °C lower melting points for the PBT. This indicates that the PBT crystals in silicon based COPEs are smaller and less perfect than in polyether (PTMO and PEO/PPO) based systems. The ability for the PBT to crystallize seems to be reduced in the PEO-PDMS-PEO based COPEs, which is also reflected in the relatively low crystallization temperatures (T_c) and the lower degree of crystallinity of PBT. While polyether-PBT block copolymers exhibit a PBT crystallinity of ca 40 %, for $(PEO\text{-}PDMS\text{-}PEO\text{-}PBT)_m$ the crystallinity was only about 25 % as determined from DSC. So far, this phenomenon cannot be explained.

Table 4. DSC data of $(PEO\text{-}PDMS\text{-}PEO\text{-}PBT)_m$.

Sample	SB [wt-%]	X_n (PBT)	T_g [°C]	T_c [°C]	T_m [°C]	ΔH [J/g]	Cryst. PBT [%]
S2	30	23	-114	160	217	24.5	24
S5	55	8	-114	131	191	16.4	25
S6	55	8	-114	122	187	17.8	27
S7	65	6	-114	79	153	8.5	17

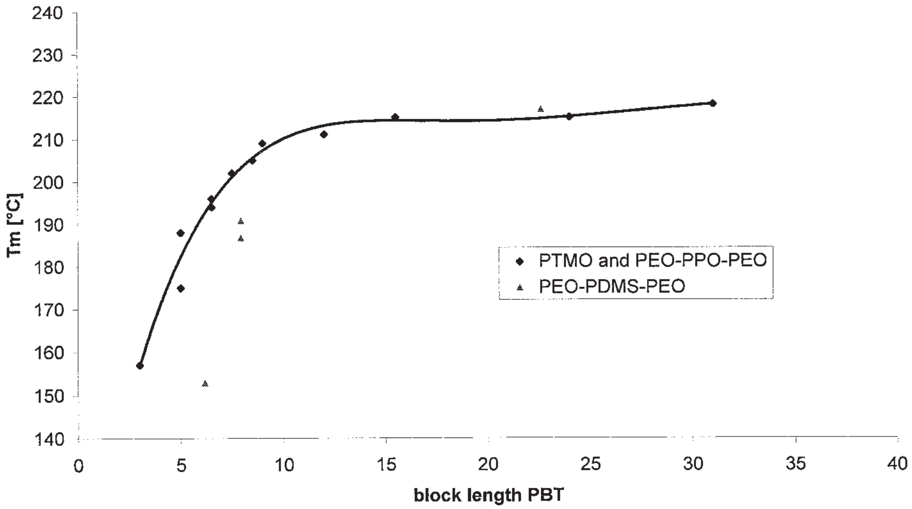

Fig. 4. T_m of the crystalline PBT with polyether and PEO-PDMS-PEO soft blocks as a function of the X_n of PBT.

2.4 Dynamic Mechanical Analysis

Figure 5 shows the results of the dynamic mechanical analysis of sample S2 with 30 wt-% of the PEO-PDMS-PEO soft block. At a temperature of –120 °C, a T_g is observed in the tan δ plot, which can be attributed to the glass transition of the almost pure PDMS phase. At 5 °C, a second transition occurs, which is linked to the T_g of a mixed amorphous phase of PBT and PEO. If the amount of soft block is increased to 55 wt-% (Figure 6), the T_g of the PDMS phase hardly shifts (-115 °C). From this, we conclude, that the PDMS phase is almost pure. In contrast, the T_g of the mixed PBT/PEO phase shifts to –48 °C due to the increase in PEO/PBT ratio.

If we compare the storage modulus E’ of the PEO-PDMS-PEO based systems with those of PEO/PPO based COPES with similar MW and same amount of soft block (Figure 5/6), we observe a lower modulus up to a temperature of –60 °C for the PEO-PDMS-PEO based COPEs, in the temperature range of –60 to +50 °C, the PEO-PDMS-PEO based COPEs show a higher modulus. Since the PDMS almost completely demixes from the PBT, it has no plasticising effect on the amorphous PBT, which could further reduce the T_g. The T_g of the system is mainly determined by the amount of PEO present.

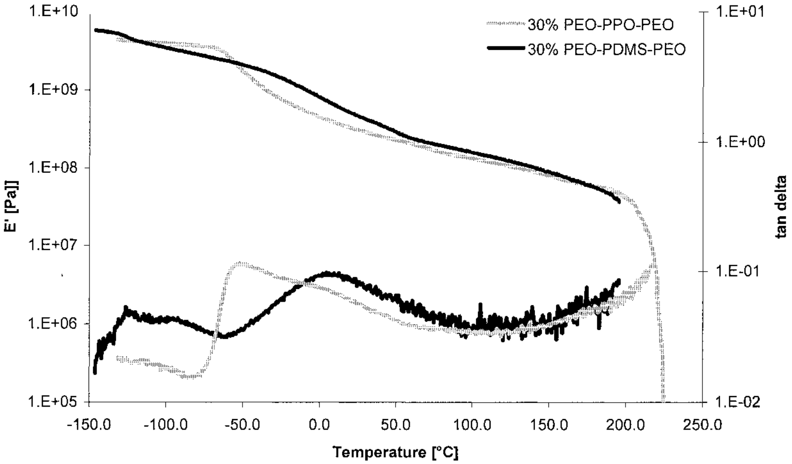

Fig. 5. DMTA of sample S2 with 30 wt-% soft block and a comparable COPE with 30 wt-% of PEO/PPO soft block.

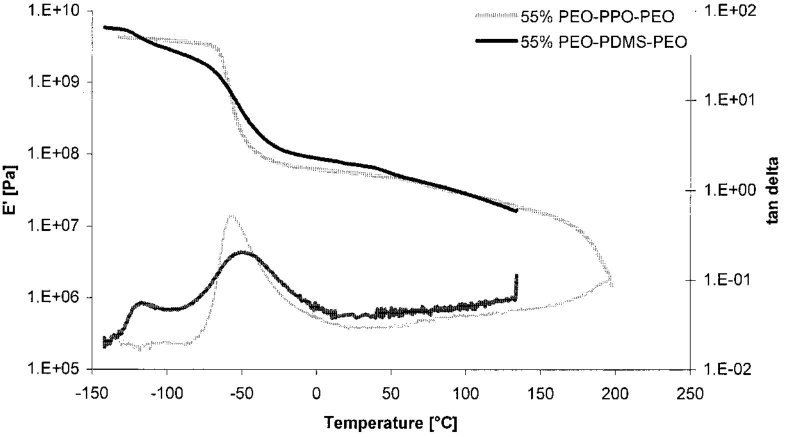

Fig. 6. DMTA of sample S6 with 55 wt-% soft block and a comparable COPE with 55 wt-% of PEO/PPO soft block.

2.5 Heat Aging

The thermo-oxidative stability in air at 135 °C has been investigated by measuring the relative solution viscosity (η_{rel}) of S1 and S2 at different times. The samples are stabilised against thermo-oxidative degradation with 0.5 wt-% of the phenolic anti-oxidant Irganox 1330. In Figure 7, η_{rel} and E_C of S1 and S2 are plotted versus the aging time.

The H-atoms in α-position next to the ether bond are labile and can react with oxygen from air. Due to chain cleavage of the ether-carbon and carbon-carbon bond formaldehyde is formed from PEO. The aldehyde will be oxidized further to formic acid, as shown in Scheme 3.[12]

$$\textbf{-O-CH}_2\textbf{-\textbackslash CH}_2\textbf{-O\textbackslash-CH}_2\textbf{-} + O_2 \rightarrow \textbf{HCOOH}$$

Scheme 3. Formation formic acid from PEO.

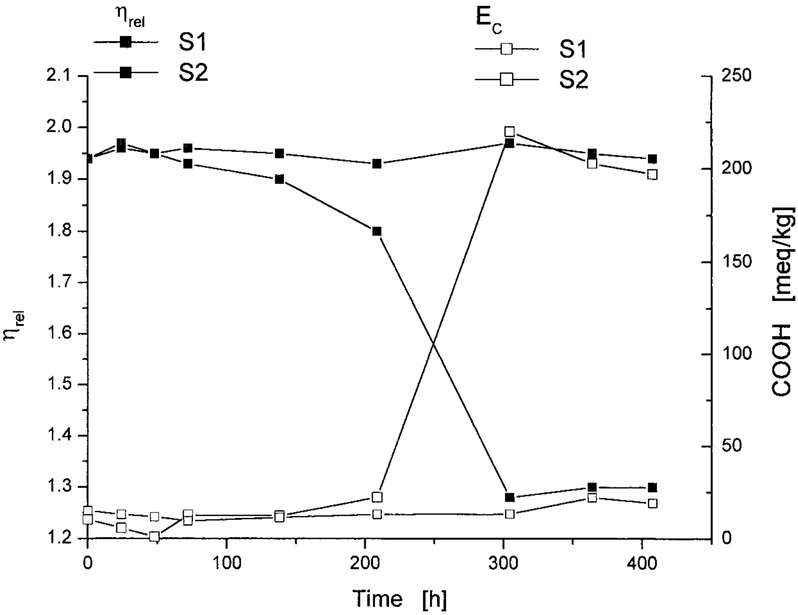

Fig. 7. η_{rel} and E_C of S1 and S2 during heat aging in air at 135 °C.

The chain cleavage causes a decrease in MW and thus η_{rel}; the formation of carboxylic acid leads to an increase in COOH. Due to the lower PEO content of S1 compared to S2, η_{rel} of S1 has not decreased after 400 h at 135 °C in air.

In Figure 8, η_{rel} of S2 and a PBT-PEO/PPO block copolymer with 30 wt-% polyether, stabilized with 0.5 wt-% Irganox 1330 during heat aging at 135 °C are shown. Due to the increased stability of PDMS compared to PPO, the thermo-oxidative stability of S1 is about 80 % higher than of PL580. Therefore, we hypothesize that an excellent heat stability should be obtained, if pure siloxane would be applied as soft block.

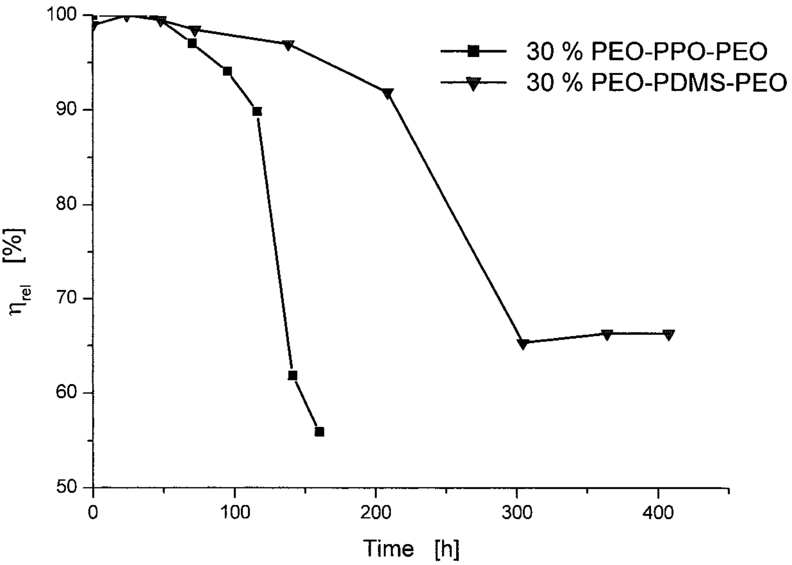

Fig. 8. η_{rel} of S2 and PBT-PEO/PPO block copolymer during heat aging in air at 135 °C.

3 Experimental Section

Materials. DMT from BP/Amoco, BDO from BASF, polysiloxane-polyether **1** from Wacker, TBT from Flucka and $Mg(OAc)_2.4H_2O$ from Aldrich were used as received.

General procedure for the preparation of (PBT-PEO-PDMS-PEO)$_m$ block copolymers, 3. DMT (330.4 g, 1.703 mol), BDO (214.6 g, 2.384 mol), **2** (440 g, 0.203 mol), TBT (383.5 mg, 1.128 mmol) $Mg(OAc)_2.4H_2O$ (241.4 mg, 1.128 mmol) and 15 droplets of silicone oil are placed in the reactor under nitrogen. The reaction mixture is heated slowly from room temperature to 220 °C under stirring and a slight nitrogen flow. The TE-reaction begins around 160 °C and methanol is distilled off. After this first step, the melt temperature is increased until 245 °C and under vacuum (< 1mbar) the distillation of BDO takes place. The PC-reaction is stopped, when the desired melt viscosity is reached. The torque is proportional to the melt viscosity and is measured by monitoring the electrical current, required to maintain an agitation rate of 20 rpm. At the end of the reaction, the melt is released from the reactor under nitrogen pressure into a water bath and rolled up to form a thread. This thread is later chopped into pellets, ready for analysis and processing.

^{1}H NMR. BRUKER Avance 500 MHz NMR spectrometer, concentration: 2% (wt/vol) in $C_2D_2Cl_4$, temperature: 80 °C, 90 ° pulse angle, 20 s relaxation delay, 128 scans, C_2HDCl_4 present in small amount in the solvent was used as an internal reference at 5.91 ppm.

^{13}C NMR. BRUKER ARX 400 NMR spectrometer under quantitative measuring conditions, concentration: 10 % (wt/vol) in $C_2D_2Cl_4$, temperature: 80 °C, 300 scans, 90 ° pulse angle, 10 s relaxation delay, inverse gated decoupling used to suppress any NOE; the internal reference: $\underline{C}_2D_2Cl_4$ at 74.2 ppm.

Viscometry. Ubbelohde capillary viscosimeter (Schott), determination of the flow time of a 10 wt-% solution with m-cresol as solvent, correction according to Hagenbach, temperature: 25 °C.

Titration of carboxylic acid end groups. Titration with potassium hydroxide, equlibrium determination with Methrohm photometer E662.

OH end groups. Esterification of the OH groups with anthracenoylchloride, high performance liquid chromatography (HPLC) of pure COPE and COPE treated with anthracenoylchloride, stainless steel column: 10 cm length, 2.1 mm ∅, 50 °C, Hypersil ODS of 5 μm particle size, UV detector, internal standard 1-hexadecanol in 1,1,1,3,3,3-hexafluoro-2-propanol; from the differences in these two chromatograms, E_{OH} is calculated.

AFM. AFM measurements were performed on a Nanoscope IIIa scanning probe microscope equipped with a J-scanner. The granulate was pressed into films using glass fiber reinforced Teflon foil (same procedure as used for DMTA measurements). Images were obtained under ambient conditions while operating the instrument in tapping mode using commercial Si cantilevers. Height and phase images were recorded simultaneously at the fundamental resonance frequency of the cantilever (typically 299-364 kHz) and at a scan speed of 0.5 lines/s (only phase images are depicted here.).

DSC. Perkin Elmer DSC7, heating and cooling rate: 20 °C min^{-1}, thermal analysis procedure: (i) heating from room temperature to 250 °C, (ii) 1 min at 250 °C, (iii) cooling from 250 °C to (-160 °C), (iv) 1 min at –160 °C, (v) heating from (– 160 °C) to 250 °C.

DMTA. Rheometrics Solids Analyser II, frequency: 1 Hz, compression molded samples with dimensions: 20 x 2 x 0.06 mm, heating rate: 5 °C/min, temperature range: -130 °C to 240 °C.

Thermo-oxidative aging. Air circulating oven (Heraeus Instruments LUT 6050E), temperature: 135 °C, granules: 2 mm ∅, 3 mm length.

4 Conclusions

(PBT-PEO-PDMS-PEO)$_m$ block copolymers have been synthesized by polycondensation of DMT, BDO and PEO-PDMS-PEO with TBT and $Mg(OAc)_2.4H_2O$ as catalysts. The soft block has been incorporated from 10 – 70 wt-%.

One major problem of polyether-PBT thermoplastic elastomers is their poor thermo-oxidative stability. Due to the excellent heat stability of PDMS, the resistance of this new thermoplastic elastomer against thermo-oxidative degradation has been increased 80 %!

The morphology of the PEO-PDMS-PEO based COPEs with a high soft block content is characterized by a crystalline PBT phase, a pure amorphous PDMS phase and a PEO/PBT mixed phase. In contrast to PTMO and PEO-PPO-PEO based COPEs, showing a co-continuous crystalline PBT phase, the crystalline PBT of the silicon Arnitels is disperse.

The melting points of the PBT in the (PBT-PEO-PDMS-PEO)$_m$ block copolymers are up to 40 °C lower than those of PTMO and PEO/PPO based COPEs. In addition, the degree of PBT crystallinity and the crystallization temperature of the PBT are also reduced.

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