New Thermoplastic Elastomers by Incorporation of Nonpolar Soft Segments in PBT-Based Copolyesters[†]

Holger Schmalz,[‡] Volker Abetz,[*,‡] Ronald Lange,[*,§] and Maria Soliman[§]

Makromolekulare Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany, and DSM Research, 6160 MD Geleen, The Netherlands

Received July 14, 2000; Revised Manuscript Received November 29, 2000

ABSTRACT: The incorporation of hydroxy-functionalized hydrogenated polybutadienes (HO−PEB−OH, KRATON liquid polymer) into PBT-based copolyesters by a conventional two-step melt polycondensation procedure is described. The usually occurring macrophase separation with nonpolar soft segments is avoided by chain extension of HO−PEB−OH with ethylene oxide to yield the corresponding hydroxy-terminated PEO−PEB−PEO triblock copolymers. Several PEO−PEB−PEO triblock copolymers with different PEO block lengths have been synthesized by means of anionic synthesis and incorporated into PBT-based copolyesters with varying PBT content. We show that the chain extension of HO−PEB−OH with ethylene oxide compatibilizes the nonpolar KRATON with the polar reactants 1,4-butanediol and dimethyl terephthalate during melt polycondensation, leading to a complete incorporation of the triblock copolymer into the copolyester. Morphological studies using SFM as well as mechanical testing show that the morphology is strongly influenced by the soft segment leading to dispersed PBT crystallites in a matrix of the soft phase. Thermal characterization of the synthesized copolyesters by DSC exhibits a low glass transition temperature and a high PBT melting point even at high soft segment contents, making these materials suitable for low- and high-temperature range applications.

Introduction

Thermoplastic elastomers combine the properties of cross-linked elastomers, such as impact-resistance and low-temperature flexibility, with the ease of processing of thermoplastic materials (extrusion, injection molding, etc.). In general, thermoplastic elastomers consist of a hard phase which provides a physical cross-linking and a soft phase providing elastic properties even at low temperatures.

Intensive studies have been done on copolyether−esters based on polybutylene terephthalate (PBT) hard segments and low molecular weight polyether soft segments like poly(ethylene oxide) (PEO), poly(tetramethylene oxide) (PTMO), or poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO−PPO−PEO) triblock copolymers.[1−4] These materials are suitable for applications in a wide temperature range due to a high PBT melting point and a low glass transition temperature of the soft phase. However, polyether soft segments tend to oxidative degradation and hydrolysis at elevated temperatures which makes the use of stabilizers necessary. To overcome these problems, saturated dimerized fatty acids were used as alternative soft segments.[5−8] The commercially available dimerized fatty acids are usually synthesized by dimerization of unsaturated C_{18} fatty acids which yields a mixture of branched C_{36} dimerized fatty acids with molecular weights of approximately 560, but there were also higher molecular C_{44} and C_{70} dimerized fatty acids used as alternative soft segments. The properties concerning thermooxidative stability were improved while the overall properties were not significantly changed.

To enhance the mechanical properties of copolyesters in terms of elasticity, it would be preferable to have a stronger phase separation between hard and soft phase and in addition a more “rubberlike” soft segment like polyolefins with low entanglement molecular weight. Not much work has been published concerning the incorporation of polyolefinic soft segments in PBT-based copolyesters. Walch et al. describe the synthesis of poly(butylene terephthalate)-*block*-polyisobutylene segmented block copolymers by using α,ω-anhydride-functionalized polyisobutylenes with molecular weights up to 3000.[9] Due to the high incompatibility of polyisobutylene with the polar reactants dimethyl terephthalate and 1,4-butanediol, phase separation occurs during the melt polycondensation process, resulting in a very poor incorporation of the soft segment. This problem was solved by using high boiling solvents like *m*-cresol and 1,2,4-trichlorobenzene, which are good solvents for PBT and polyisobutylene. The solvent was then removed together with surplus 1,4-butanediol in the polycondensation step by applying vacuum during polymerization. Nevertheless, there is some macrophase separation in the second step of the polycondensation when most of the solvent is evaporated. This macrophase separation is responsible for the relatively high amount of extractable polyisobutylene for copolyesters with high soft segment content. Kennedy et al. describe a similar solvent-based approach for the synthesis of poly(butylene terephthalate)-*block*-polyisobutylene using hydroxy telechelic polyisobutylenes with molecular weights up to 10 000.[10] In both contributions only little information is given with regard to the mechanical properties of these systems. Mechanical testing results in poor mechanical properties probably due to incomplete incorporation of the nonpolar polyisobutylene and inhomogeneities in the material arising from insufficient stirring during synthesis.

So far it has not been possible to incorporate polyolefinic soft segments by conventional melt polycondensation processes due to the above-mentioned macro-

---

[‡] Universität Bayreuth.
[§] DSM Research.
[†] In Memoriam Prof. Dr. Reimund Stadler.

10.1021/ma001226p CCC: $20.00

phase separation. The macrophase separation can be avoided by using cosolvents during the synthesis. However, this is not acceptable for processing and environmental reasons. An alternative way of preventing the macrophase separation during melt polycondensation could be an anionic chain extension of KRATON (HO−PEB−OH) with ethylene oxide. This results in the corresponding poly(ethylene oxide)-*block*-poly(ethylene-*stat*-butylene)-*block*-poly(ethylene oxide) triblock copolymers where the PEO blocks should compatibilize the nonpolar KRATON with the polar reactants dimethyl terephthalate and 1,4-butanediol during melt polycondensation. This leads to a homogeneous reaction mixture which is necessary to obtain high molecular weight copolyesters with good mechanical properties. Here, we present a new method for the synthesis of polyesters with polyolefinic soft segments based on hydroxy telechelic hydrogenated polybutadienes (HO−PEB−OH, KRATON liquid polymer HPVM-2203) by a conventional melt polycondensation procedure without using any cosolvents.

Experimental Section

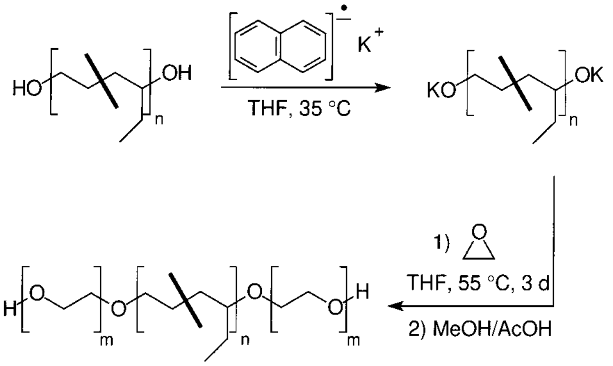
Materials. Tetrahydrofuran (Merck) was purified by successive distillation over CaH_2 and potassium. Ethylene oxide (Linde) was condensed onto CaH_2 and stirred at 0 °C for 3 h before being transferred into glass ampules. KRATON liquid polymer HPVM-2203 (Shell) was purified by freeze-drying with benzene for at least three times followed by drying under high vacuum at 60 °C for 2 days. Naphthalene (Bayer) was purified by sublimation and stored under nitrogen until use. Potassium naphthalide solutions were synthesized by reaction of naphthalene with potassium in THF under nitrogen. The green color of potassium naphthalide appeared immediately, and the reaction mixture was allowed to stir overnight at room temperature before use. The solutions had a typical concentration of 0.5 mol/L and could be stored in a freezer for several weeks.

Dimethyl terephthalate (Fluka), 1,4-butanediol (Fluka), and tetrabutyl orthotitanate (Fluka) were used without further purification.

Synthesis of PEO−PEB−PEO Triblock Copolymers. The synthesis of PEO−PEB−PEO triblock copolymers was accomplished by anionic ring-opening polymerization of ethylene oxide in THF using HO−PEB−OH (KRATON liquid polymer HPVM-2203) with a molecular weight of 3600 as starting material. The terminal hydroxy groups of HO−PEB−OH were first deprotonated by titration with a 0.5 M solution of potassium naphthalide at 35 °C to yield the corresponding bifunctional macroinitiator KO−PEB−OK.[11−13] The titration was stopped after the slight green color of excess potassium naphthalide remains for at least 45 min. After addition of ethylene oxide at 0 °C the polymerization was carried out at 55 °C for 3−4 days. The reaction was terminated with acetic acid/methanol (5:1 by vol), and the products were precipitated in petrol ether (bp 40−60 °C, M_n(PEO) > 1400 g/mol) or acetone at −30 °C (M_n(PEO) < 1400 g/mol).

Synthesis of Copolyesters. The synthesis of copolyesters based on PEO−PEB−PEO soft segments was accomplished by using common two-step melt polycondensation procedures.[3] The reaction was carried out in a cylindrical flask with nitrogen inlet, mechanical stirrer, and distillation bridge. In the first step a mixture of PEO−PEB−PEO triblock copolymer, dimethyl terephthalate, 1,4-butanediol (50% molar excess with regard to the methyl ester units), a phenolic antioxidant, and tetrabutyl orthotitanate (1.42 mmol/kg polymer) as a solution in 1,4-butanediol was heated for 1 h to 190, 200, and 210 °C, respectively, under nitrogen in order to distill off the methanol. Then the temperature was raised stepwise to 230 and 250 °C, and vacuum (0.05−0.1 mbar) was applied for 2.5 h after reaching 230 °C.

Scheme 1. Synthesis of Poly(ethylene oxide)-*block*-poly(ethylene-*stat*-butylene)-*block*-poly(ethylene oxide) Triblock Copolymers



Measurements. Size exclusion chromatography (SEC) experiments were performed on a Waters instrument calibrated with polystyrene standards at 30 °C. Four PSS−SDV columns (5 μm, Polymer Standards Service, Mainz) with a porosity range from 10^2 to 10^5 Å were used together with a differential refractometer and a UV detector. Measurements on the PEO−PEB−PEO triblock copolymers were performed in THF with a flow rate of 1 mL/min using toluene as internal standard. For thermal analysis a Perkin-Elmer DSC 7 with a CCA 7 liquid nitrogen cooling device was used. For all measurements a two-point calibration with chloroform and indium was applied. All experiments were performed at heating rates of 20, 30, and 40 K/min. Given transition temperatures correspond to an extrapolated heating rate of 0 K/min, heat of fusions refer to a heating rate of 20 K/min unless otherwise specified. The displayed heat flow traces correspond to a heating rate of 20 K/min (second heating run). Mechanical testing was performed on an Instron 5565 tensile testing machine at room temperature. The Young's modulus was determined at a testing speed of 0.2 mm/s at small elongations (up to 3−4%); elongations at break were measured at 20 mm/s. For ^1H NMR measurements a Bruker AC 250 spectrometer was used. For small-angle X-ray scattering (SAXS) a Bruker AXS-Nanostar with sealed tube (Cu), crossed Göbel mirrors, 2-dimensional Hi-Star detector, and temperature controlling unit was used. The SFM image was taken from melt-pressed films using Teflon plates on a Digital Instruments Nanoscope IIIa operated in Tapping Mode.

Results and Discussion

The preparation of PEO−PEB−PEO triblock copolymers involves in the first step the transfer of the starting material HO−PEB−OH (M_n = 3600 g/mol, OH functionality = 1.9) to the corresponding bifunctional macroinitiator KO−PEB−OK for the anionic ring-opening polymerization of ethylene oxide. This was accomplished by titration of a HO−PEB−OH solution in dry tetrahydrofuran with potassium naphthalide solution under nitrogen. The intensive green color of potassium naphthalide allows a very precise end-point determination which is indispensable in order to avoid the formation of homo-PEO during ethylene oxide polymerization initiated by excess potassium naphthalide. The titration was carried out at 35 °C due to precipitation of associates at lower temperatures when approaching the end point of titration. Ethylene oxide polymerization was performed at 55 °C in tetrahydrofuran for 3−4 days to give the corresponding hydroxy-terminated PEO−PEB−PEO triblock copolymers (Scheme 1). Because of the strong association of potassium alkoxides, the concentration of active centers had to be kept low ($<1 \times 10^{-2}$ mol/L) in order to avoid

Table 1. Molecular Weights and Polydispersities of PEO−PEB−PEO Triblock Copolymers

sample	$M_{n,SEC}$[a] [g/mol]	$M_{n,NMR}$ [g/mol]	$M_n(PEO)_{NMR}$ [g/mol]	M_w/M_n
HO−PEB−OH	7 990	3600[b]	−	1.09
$PEO_{36}-PEB_{28}-PEO_{36}^{12.8}$	16 420	12800	4600	1.13
$PEO_{29}-PEB_{42}-PEO_{29}^{8.6}$	13 820	8620	2510	1.08
$PEO_{27}-PEB_{46}-PEO_{27}^{8.0}$	13 190	7980	2190	1.08
$PEO_{25}-PEB_{50}-PEO_{25}^{7.1}$	11 930	7060	1730	1.09
$PEO_{22}-PEB_{56}-PEO_{22}^{6.4}$	11 580	6360	1380	1.08
$PEO_{18}-PEB_{64}-PEO_{18}^{5.6}$	10 080	5600	1000	1.11
$PEO_{16}-PEB_{68}-PEO_{16}^{5.2}$	9 570	5240	820	1.12

[a] Determined by SEC in THF, calibrated against polystyrene standards. [b] Determined by end group analysis.

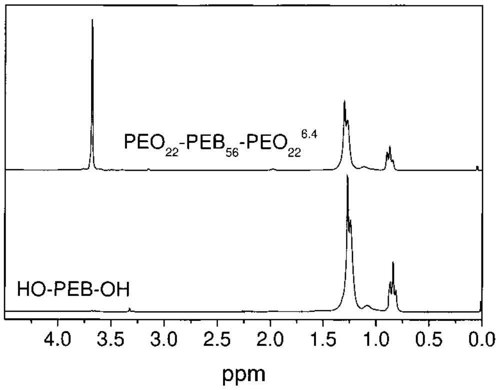


Figure 1. The 250 MHz ^{1}H NMR spectra of the starting material HO−PEB−OH and the triblock copolymer $PEO_{22}-PEB_{56}-PEO_{22}^{6.4}$ in $CDCl_3$.

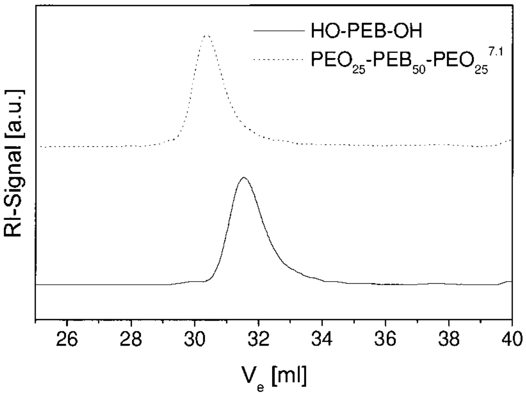


Figure 2. SEC traces of HO−PEB−OH and the triblock copolymer $PEO_{25}-PEB_{50}-PEO_{25}^{7.1}$ using THF as eluent and toluene as internal standard.

Table 2. DSC Data of PEO−PEB−PEO Triblock Copolymers[a]

sample	M_n(PEO) [g/mol]	T_m [°C]	T_C[b] [°C]	α(PEO) [%]	T_G [°C]
$PEO_{36}-PEB_{28}-PEO_{36}^{12.8}$	4600	53.7	18.3	78.0	−61.9
$PEO_{29}-PEB_{42}-PEO_{29}^{8.6}$	2510	44.3	6.3	75.2	−63.8
$PEO_{27}-PEB_{46}-PEO_{27}^{8.0}$	2190	39.7	9.9	73.3	−66.1
$PEO_{25}-PEB_{50}-PEO_{25}^{7.1}$	1730	38.3	5.4	73.8	−64.3
$PEO_{22}-PEB_{56}-PEO_{22}^{6.4}$	1380	35.9	2.5	74.3	−62.2
$PEO_{18}-PEB_{64}-PEO_{18}^{5.6}$	1000	29.8	−28.3	60.3	−60.9
$PEO_{16}-PEB_{68}-PEO_{16}^{5.2}$	820	24.4	−31.2	60.1	−61.2

[a] T_m = melting point, T_C = crystallization temperature, α = degree of crystallinity, and T_G = glass transition temperature. [b] Measured at a cooling rate of 40 K/min.

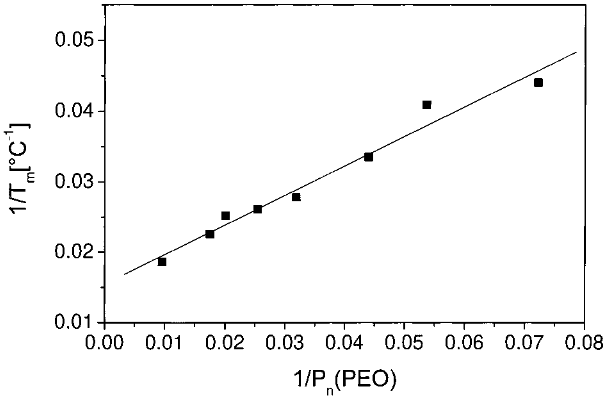


Figure 3. Dependence of $1/T_m$(PEO) on $1/P_n$(PEO) for the synthesized PEO−PEB−PEO triblock copolymers.

precipitation of associates. The use of cryptands like C222 to suppress association is not necessary in this case and furthermore do not effect the molecular weight distribution. Different $PEO_xPEB_yPEO_x^m$ triblock copolymers (the subscripts x and y give the weight percentage of the corresponding block, and the superscript m is the molar mass of the triblock copolymer in kg/mol) with PEO block lengths between 800 and 4600 g/mol have been synthesized and characterized by ^{1}H NMR spectroscopy and SEC (Table 1, Figure 1). Size exclusion chromatography measurements in tetrahydrofuran show that the chain extension of HO−PEB−OH with ethylene oxide yields narrow distributed triblock copolymers ($1.08 < M_w/M_n < 1.13$) without residual starting material and homo-PEO impurities (Figure 2). The SEC trace of the triblock copolymer exhibits a small tailing at the lower molecular weight side which can also be seen for HO−PEB−OH. This can be attributed to monofunctional or not functionalized components in HO−PEB−OH which exhibits an OH-functionality of only 1.9.

The results of thermal analysis on the PEO−PEB−PEO triblock copolymers are listed in Table 2. All triblock copolymers show one glass transition temperature at −61 to −66 °C corresponding to the PEB middle block and amorphous poly(ethylene oxide). A differentiation between T_G(PEB) and T_G(PEO) is not possible probably due to overlapping transition temperatures, resulting in a broad glass transition region. The degree of crystallinity for poly(ethylene oxide) is nearly constant for $M_n(PEO) \geq 1380$ g/mol (α ∼ 75%) and decreases for smaller PEO block lengths. The degree of crystallinity was calculated assuming a heat of fusion for PEO of $\Delta H_m^0 = 196.6$ J/g.[14] The investigated triblock copolymers exhibit a strong dependence between the melting point of crystallizable PEO blocks and the average degree of polymerization P_n(PEO). Figure 3 shows a plot of $1/T_m$(PEO) vs $1/P_n$(PEO) demonstrating the linear dependence of $1/T_m$ on $1/P_n$ for the synthesized triblock copolymers.

The synthesis of copolyesters with PEO−PEB−PEO soft segments was accomplished by using a conventional two-step melt polycondensation procedure using tetrabutyl orthotitanate as catalyst. For materials with good elastic properties it is crucial that the soft segment, providing the elastic properties, forms the matrix, and the crystalline PBT domains are dispersed within the matrix. Therefore, we focused on the investigation of copolyesters with soft segment contents ≥50 wt %. Several copolyesters with PBT contents between 10 and 50 wt % and different PEO−PEB−PEO soft segments (varying M_n(PEO)) have been synthesized (Table 3). Copolyesters with PBT contents >45 wt % and molecular weights of the soft segments ≥7000 g/mol (M_n(PEO) ≥ 1700 g/mol) exhibit a turbid melt during melt poly-

Table 3. Data of Synthesized Copolyesters

sample	*w*(PBT) [%]	M_n(PEO) [g/mol]	x_{HS}[a]	l_{HS}[b]	melt	code
1	50	4600	0.983	58.3	turbid	PBT50-4600
2	50	2510	0.975	40.1	turbid	PBT 50-2510
3	50	2190	0.973	37.2	turbid	PBT 50-2190
4	50	1730	0.970	33.0	turbid	PBT 50-1730
5	40	2510	0.963	27.1	slightly turbid	PBT 40-2510
6	40	2190	0.960	25.1	slightly turbid	PBT 40-2190
7	40	1730	0.955	22.4	slightly turbid	PBT 40-1730
8	40	1380	0.951	20.2	clear	PBT 40-1380
9	30	1380	0.925	13.4	clear	PBT 30-1380
10	20	1380	0.878	8.2	clear	PBT 20-1380
11	45	1000	0.954	21.8	clear	PBT 45-1000
12	40	1000	0.944	17.9	clear	PBT 40-1000
13	35	1000	0.932	14.7	clear	PBT 35-1000
14	30	1000	0.916	11.9	clear	PBT 30-1000
15	25	1000	0.894	9.5	clear	PBT 25-1000
16	20	1000	0.864	7.4	clear	PBT 20-1000
17	10	1000	0.739	3.8	clear	PBT 10-1000
18	40	820	0.941	16.9	clear	PBT 40-820
19	30	820	0.911	11.2	clear	PBT 30-820

[a] Mole fraction of hard segment (PBT). [b] Average segment length of the hard segment calculated according to $l_{HS} = 1/(1 - x_{HS})$.

condensation, indicating a phase separation in the melt. This might be due to the high content of polar monomers in the reaction mixture and the high molecular weight of the soft segment. All other copolyesters show a clear melt during the synthesis; i.e., the reaction mixture is homogeneous, and no macrophase separation occurs. The incorporation of the PEO−PEB−PEO triblock copolymer into the polyester can be confirmed by successive Soxhlet extraction of the copolyesters with chloroform and tetrahydrofuran. For PBT50-2190 Soxhlet extraction yields only 4 wt % THF-soluble extract, confirming the almost complete incorporation of the soft segment, even for systems exhibiting turbid melts during melt polycondensation. In addition, SEC analysis of the extract, compared with the used soft segment, shows that the extract contains only negligible amounts of pure triblock copolymer; i.e., most of the soluble components contain soft segment with short PBT blocks. From these measurements it can be concluded that chain extension of HO−PEB−OH with ethylene oxide is a very useful method to incorporate nonpolar soft segments into polyesters without using any cosolvents in the first step of the melt polycondensation.

Characterization of the copolyesters by SFM shows the typical TPE morphology with well phase separated hard and soft phases as depicted in Figure 4. The bright longish domains correspond to PBT crystallites which exhibit a higher phase contrast compared to the more softer soft segment phase. The PBT crystallites are dispersed within a matrix of the soft segment and exhibit a broad crystallite size distribution. The darker regions, representing the soft segment phase, show a microstructure arising from the microphase separation of the incorporated PEO−PEB−PEO triblock copolymer. Taking into account that the PEO blocks in PBT20-1000 are molten at room temperature, the structure of the incorporated triblock copolymer $PEO_{18}-PEB_{64}-PEO_{18}$[5,6] was investigated by small-angle X-ray scattering. The semilogarithmic SAXS profile at 80 °C (molten PEO blocks) exhibits reflex positions at a ratio of $1{:}\sqrt{3}{:}2{:}\sqrt{7}$ which are typical for hexagonally packed cylinders (Figure 5). In conclusion, the microstructure of the soft segment phase in PBT20-1000 might be attributed to a distorted cylindrical structure with the bright spots referring to PEO cylinders. As SAXS is a very useful method for investigating the morphology of the PEO−PEB−PEO soft segments, we also performed measurements on the synthesized copolyesters. Unfortunately, the experiments do not give sufficient information for structure elucidation.

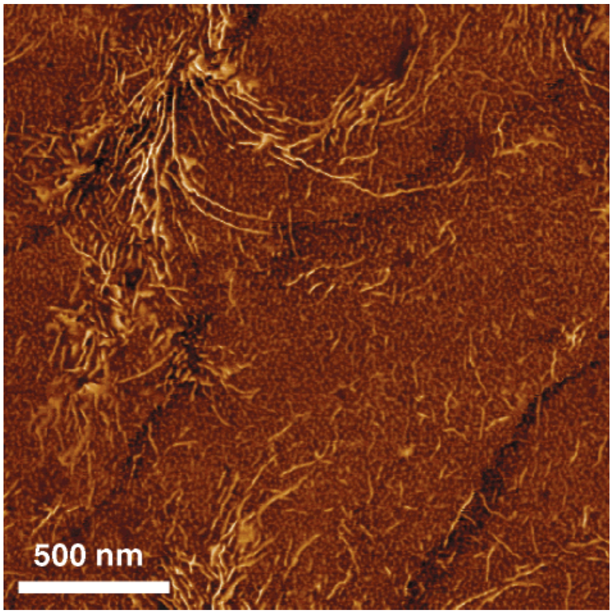


Figure 4. SFM phase image of a melt-pressed film of PBT20-1000 onto a glass wafer; *z* range 40°.

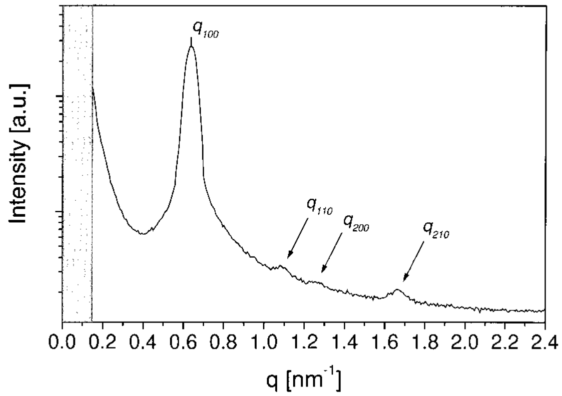


Figure 5. Semilogarithmic SAXS profile for the triblock copolymer $PEO_{18}-PEB_{64}-PEO_{18}$[5,6] at 80 °C (scattering vector $q = 4\pi/\lambda \sin \Theta$ with 2Θ being the scattering angle and $\lambda = 0.1542$ nm).

Table 4. DSC Data of Copolyesters[a]

	T_m(PEO) [°C]	T_c(PEO) [°C]	T_{rc}(PEO) [°C]	α(PEO) [%]	T_m(PBT) [°C]	T_{c1}(PBT)[b] [°C]	T_{c2}(PBT)[b] [°C]	T_{c3}(PBT)[b] [°C]	α(PBT) [%]	T_G [°C]
PBT40-2510	23.8	−14.9	–	16.5	210.2	–	90.5	33.1	21.5	−65.7
PBT40-2190	25.7	−16.7	–	14.3	215.7	–	92.7	41.0	18.7	−59.1
PBT40-1730	12.5	−37.4	–	12.4	208.8	–	85.6	37.3	17.5	−65.5
PBT40-1380	7.0	−49.2	−46.3	8.1	207.7	–	78.3	46.5	15.8	−66.1
PBT30-1380	3.8	–	−47.6	7.9	202.5	–	74.7	53.3	24.0	−66.5
PBT20-1380	13.5	−42.3	−40.6	9.6	184.0	–	–	51.8	21.9	−60.3
PBT45-1000	6.1	–	−35.2	3.7	217.5	–	93.3	58.3	27.3	−57.6
PBT40-1000	3.4	–	−36.0	3.7	211.4	–	89.9	52.6	21.8	−58.2
PBT35-1000	4.2	−46.4	−35.2	3.9	213.5	–	89.9	54.3	23.3	−58.0
PBT30-1000	4.9	−45.7	−32.9	4.0	212.1	126.3	85.9	58.3	27.8	−58.1
PBT25-1000	10.8	−46.7	−41.9	9.8	214.9	136.3	83.6	60.6	31.1	−59.1
PBT20-1000	5.5	−46.7	−38.5	8.3	190.0	–	–	60.6	27.0	−59.8
PBT10-1000	8.5	–	−31.5	6.3	–	–	–	–	–	−59.5
PBT40-820	–	–	–	–	213.8	–	81.4	–	24.4	−59.9
PBT30-820	–	–	–	–	212.4	–	81.7	44.9	16.0	−59.7

[a] T_m = melting temperature, T_c = crystallization temperature, T_{rc} = recrystallization temperature, α = degree of crystallinity, and T_G = glass transition temperature. [b] Crystallization temperatures refer to a cooling rate of 20 K/min for PBTx-1000 and 40 K/min for all other samples.

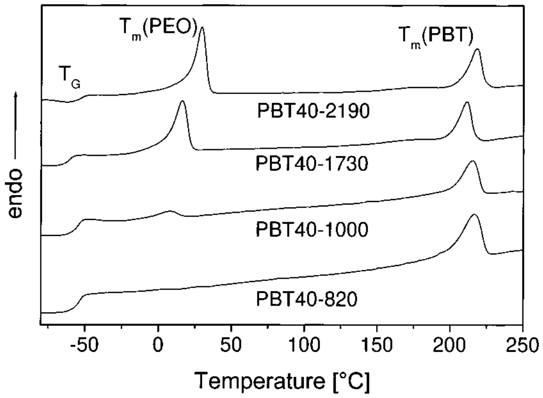


Figure 6. Thermal properties of copolyesters in dependence of the incorporated soft segment.

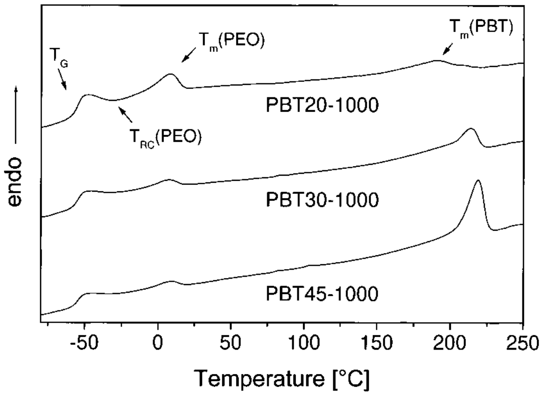


Figure 7. Thermal properties of copolyesters in dependence of the hard segment content.

The DSC data of some representative copolyesters are given in Table 4. The degree of crystallinity for PBT was calculated using a heat of fusion of $\Delta H_m^0 = 145.3$ J/g.[15] The detected glass transition temperatures are only slightly shifted compared to the glass transition temperatures of the pure triblock copolymers and are almost independent of composition, indicating a pronounced microphase separation in the soft phase. A glass transition temperature of pure amorphous PBT cannot be seen in the heat flow traces, probably due to partial mixing of amorphous PBT and PEO, although a glass transition temperature of a mixed amorphous PBT/PEO phase is also not detectable. Usually the copolyesters exhibit a melting endotherm corresponding to crystalline PEO and PBT (Table 4, Figure 6). Only for systems with very short PEO blocks like PBT40-820 and PBT30-820 no melt transition for PEO is observed; i.e., in these systems the poly(ethylene oxide) blocks are not able to form crystalline domains. The melting points and degrees of crystallinity of PEO blocks in copolyesters are shifted to lower values compared to the pure soft segment (Tables 2 and 4). Upon cooling the PBT segments crystallize and predefine the morphology. The crystallization of PEO which appears at much lower temperatures is influenced by the existing morphology, leading to smaller and less perfect crystallites. This shift in the PEO melting endotherm and degree of crystallinity also confirms the incorporation of the triblock copolymer soft segment into the polyester. Figure 7 shows some copolyesters with $PEO_{18}-PEB_{64}-PEO_{18}{}^{5.6}$ soft segments and varying PBT content. As the melting point of the hard segment in copolyesters strongly depends on its average segment length $l_{HS} = 1/(1 - x_{HS})$, where x_{HS} = mole fraction of PBT hard segment, the PBT melting point decreases with increasing soft segment content.[16] In addition, a broadening of the PBT melting endotherm can be observed with decreasing PBT content, indicating a broadening of the crystallite size distribution. The latter was also detected by SFM investigations (Figure 4). Especially copolyesters with high soft segment content and low molecular weight PEO segments like PBT20-1000 exhibit crystallization of the PEO segments upon heating. In these systems the PEO crystallization is hindered upon cooling which leads to recrystallization upon heating followed by melting of the formed metastable crystals. Compared to conventional copolyether−ester with low molecular weight polyether soft segments like poly(tetramethylene oxide), the PBT melting point in our systems is much higher at the same soft segment content, which can be attributed to a higher hard segment block length.[17,18] Together with the low glass transition temperature, the high PBT melting point enables the application of these copolyesters in a wide temperature range.

Mechanical testing was performed on melt-pressed test samples with an average size of 1.0 cm × 4.8 cm (Table 5). Figure 8 shows the stress−strain traces of copolyesters with $PEO_{18}-PEB_{64}-PEO_{18}{}^{5.6}$ soft segments measured at room temperature. The stress−strain behavior is typical for elastic materials. All samples

Table 5. Mechanical Properties of Copolyesters with $PEO_{18}-PEB_{64}-PEO_{18}{}^{5.6}$ Soft Segments[a]

sample	*E* [GPa]	σ_B [MPa]	ϵ_B [%]
PBT40-1000	1.27×10^{-2} (5.7×10^{-4})	11.0 (1.3)	370 (99)
PBT30-1000	1.05×10^{-2} (7.3×10^{-4})	10.8 (0.4)	670 (57)
PBT20-1000	7.02×10^{-3} (1.3×10^{-3})	9.31 (0.5)	980 (55)
PBT10-1000	3.94×10^{-3} (1.1×10^{-4})	3.72 (0.3)	450 (58)
PBT40-820	1.87×10^{-2} (3.1×10^{-3})	11.4 (1.2)	400 (50)
PBT30-820	1.31×10^{-2} (1.8×10^{-3})	8.98 (0.4)	490 (37)

[a] E = Young's modulus, σ_B = stress at break, and ϵ_B = elongation at break; the values in parentheses give the standard deviations (derived from at least three experiments).

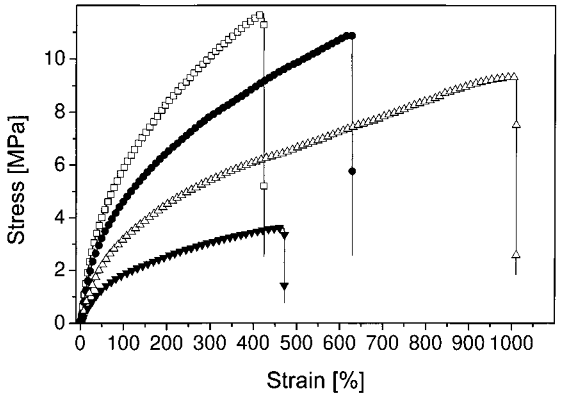


Figure 8. Stress−strain traces for copolyesters with $PEO_{18}-PEB_{64}-PEO_{18}{}^{5.6}$ soft segments: (□) PBT40-1000, (●) PBT30-1000, (△) PBT20-1000, (▼) PBT10-1000.

show a lack of yielding, indicating a dispersed PBT phase within a matrix of soft segment, as also detected by SFM measurements (Figure 4). The elongation at break increases with increasing soft segment content up to ~1000% for PBT20-1000 (Figure 8). A further increase in the soft segment content (PBT10-1000) results in a smaller elongation at break, probably due to the low crystallinity of PBT in this sample (Table 4, T_m(PBT) not detectable). In the range of soft segment contents of 60−90% the Young's modulus exhibits a linear decrease with increasing soft segment content whereas the stress at break decreases significantly above a soft segment content of about 80% (Figure 9).

Conclusion

We have shown for the first time that the incorporation of polyolefinic soft segments like HO−PEB−OH (KRATON liquid polymer HPVM-2203) in PBT-based copolyesters by a conventional two-step melt polycondensation is possible without using any cosolvents by chain extension of the soft segment with ethylene oxide. The resulting amphiphilic PEO−PEB−PEO triblock copolymers are able to dissolve in a mixture of dimethyl terephthalate and 1,4-butanediol during melt polycondensation. This leads to a homogeneous reaction mixture and a quantitative incorporation of the soft segment. The synthesized copolyesters exhibit low glass transition temperatures combined with high PBT melting points even at high soft segment contents, making these polymers suitable for low- and high-temperature range applications. The mechanical properties, e.g. Young's modulus and elongation at break, can be adjusted to product requirements by varying the soft segment content. Depending on the composition, elongations at break up to 1000% can be achieved with these materials. Further investigations on elastic properties and morphology are in progress and will be published elsewhere.

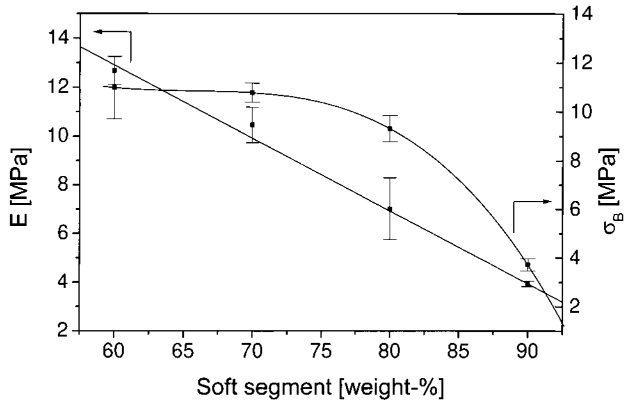


Figure 9. Young's modulus E and stress at break σ_B in dependence of the soft segment content for copolyesters with $PEO_{18}-PEB_{64}-PEO_{18}{}^{5.6}$ soft segments.

Acknowledgment. The authors are very grateful to Reimund Stadler, who initiated this work. Also, the fruitful discussions with many colleagues at the University of Bayreuth and DSM Research are acknowledged. We especially like to thank B. Goderis for the SFM measurements, K. Loos for help with DSC measurements, and S. Stangler for assistance with SAXS investigations.

References and Notes

(1) Legge, N. R.; Holden, G.; Schroeder, H. E. *Thermoplastic Elastomers, A Comprehensive Review*; Hanser: Munich, 1987.
(2) Cella, R. J. *J. Polym. Sci., Polym. Symp.* **1973**, *42*, 727.
(3) Hoeschele, G. K.; Witsiepe, W. K. *Angew. Makromol. Chem.* **1973**, *29/30*, 267.
(4) Hoeschele, G. K. *Chimia* **1974**, *28*, 544.
(5) Hoeschele, G. K. *Angew. Makromol. Chem.* **1977**, *58/59*, 299.
(6) Manuel, H. J.; Gaymans, R. J. *Polymer* **1993**, *34*, 636.
(7) Manuel, H. J.; Gaymans, R. J. *Polymer* **1993**, *34*, 4325.
(8) Fray, M. E.; Slonecki, J. *Kautsch. Gummi Kunstst.* **1996**, *49*, 692.
(9) Walch, E.; Gaymans, R. J. *Polymer* **1994**, *35*, 636.
(10) Deák, G.; Kennedy, J. P. *Macromol. Rep.* **1996**, *A33 (Suppls. 7&8)*, 439.
(11) Bayer, U.; Stadler, R. *Macromol. Chem. Phys.* **1994**, *195*, 2709.
(12) Hillmyer, M. A.; Bates, F. S. *Macromolecules* **1996**, *29*, 6994.
(13) Allgaier, J.; Poppe, A.; Willner, L.; Richter, R. *Macromolecules* **1997**, *30*, 1582.
(14) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1980; Vol. 3, p 67.
(15) Van Krevelen, D. W. *Properties of Polymers*, 2nd ed.; Elsevier: Oxford, 1976; p 578.
(16) Frensdorff, H. K. *Macromolecules* **1971**, *4*, 369.
(17) Baik, D. H.; Lee, M. S.; Jeon, B. Y.; Han, M. S. *J. Korean Fiber Soc.* **1994**, *31*, 613.
(18) Cella, R. J. Polyesters, Elastomeric. In *Encyclopedia of Polymer Science and Technology*; Interscience Publishers: New York, 1977; Suppl. Vol. 2.

MA001226P