Synthesis and Characterization of Novel Thermoplastic Polyester Containing Blocks of Poly[(*R*)-3-hydroxyoctanoate] and Poly[(*R*)-3-hydroxybutyrate]

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ABSTRACT: Novel block copolyester containing biocompatible and biodegradable biopolyester blocks was prepared by polycondensation of telechelic hydroxylated poly[(*R*)-3-hydroxyoctanoate] (PHO-diol) and telechelic hydroxylated poly[(*R*)-3-hydroxybutyrate] (PHB-diol) with terephthaloyl chloride (TeCl). Reaction of PHO-diol (M_p of 2100), PHB-diol (M_p of 3200), and TeCl at a ratio of 1.3:1:2.1 gave the block co-polyester PHOHBTe in 86% yield with a molecular weight M_p of 7200 (GPC). The chemical structure of the copolyester was confirmed by ^{1}H-, ^{13}C-, and COSY-NMR and IR spectra. On average, 2 PHO-diol, 1 PHB-diol, and 2 TeCl were incorporated in each molecule of the block copolyester PHOHBTe. For comparison, polyester PHOTe with a M_p of 7100 (GPC) was prepared in 81% yield by reaction of PHO-diol and terephthaloyl chloride at a molar ratio of 1:1.2. NMR analysis suggested that PHOTe contains 3 PHO and 3 Te units on average. While PHOTe containing no PHB block is soft-sticky, PHOHBTe containing both soft PHO and hard PHB blocks showed good thermoplastic properties with T_m of 129 and 140 °C and a T_g of −41 °C. Thus, for the first time, block copolyester containing PHO and PHB blocks has been prepared and demonstrated to be thermoplastic.

Introduction

The microbial poly[(*R*)-3-hydroxyalkanoates] (PHAs) are potentially very useful materials due to their biodegradability and biocompatibility. Their thermal properties are, however, rather poor: poly[(*R*)-3-hydroxybutyrate] (PHB) is crystalline-brittle with a melting temperature (T_m) of 175 °C and a glass transition temperature (T_g) of 0−4 °C;[1−4] mcl-PHAs (which contain medium chain length alkanoate monomers) are weakly crystalline and soft-sticky with T_m between 39 and 61 °C and T_g between −25 and −44 °C.[5−10] A way to improve the thermoplastic properties of PHAs is to make a copolyester. Biosyntheses of random copolyesters such as poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyvalerate], P(3HB-*co*-3HV),[2,11−13] and poly[(*R*)-3-hydroxybutyrate-*co*-(*R*)-3-hydroxyalkanoate], P(3HB-*co*-3HA),[14−17] are known. Among them, P(94%3HB-*co*-6%3HA) consisting of 94% monomers of (*R*)-3-hydroxybutyrate (3HB) and 6% monomers of (*R*)-3-hydroxyalkanoates (3HA) containing 6−12 carbon atoms showed interesting thermoplastic properties with a T_g of −8 °C and T_m of 133 and 146 °C.[16]

We are interested in chemical preparation of block copolyesters from PHAs for desired thermal and mechanical properties. Recently, we transformed mcl-PHAs into enantiomerically pure telechelic hydroxylated mcl-PHAs (mcl-PHA-diols) with low molecular weight, low T_m, and low T_g.[18] The easily available telechelic hydroxylated poly[(*R*)-3-hydroxyoctanoate] (PHO-diol) was demonstrated to be an excellent soft segment for copolymerization.[19] On the other hand, telechelic hydroxylated poly[(*R*)-3-hydroxybutyrate] (PHB-diol)[20] was shown to be a useful hard segment.[21,19] Thus, it might be possible to prepare block copolyesters with good thermoplastic properties by incorporating the soft PHO-diol and the hard PHB-diol into the polymer. Moreover, the polymer properties might be designed and then achieved by changing the ratio of the soft and hard segments. Here, we report the first synthesis of block co-polyesters containing PHO and PHB blocks by polymerization of the soft segment PHO-diol and the hard segment PHB-diol with terephthaloyl chloride, the analysis of the polymer structures, and the characterization of the physical properties.

Experimental Section

Materials. Telechelic hydroxylated poly[(*R*)-3-hydroxyoctanoate] containing C8 and C6 monomers in a ratio of 90:10 [PHO-diol, M_n = 2400 (VPO), M_p = 2100 (GPC)][18] and telechelic hydroxylated poly[(*R*)-3-hydroxybutyrate] [PHB-diol, M_n = 2600 (VPO), M_p = 3200 (GPC)][20] were prepared according to the published procedures and predried by azeotropic distillation with 1,2-dichloroethane. All reagents and solvents were purchased from Fluka with p.a. quality: terephthaloyl chloride was dried under high vacuum at room temperature for 2 days before use; pyridine, toluene, and chloroform were dried with activated molecular sieve A4 (pore size 4 Å).

Synthesis of Block Copolyester PHOHBTe. Toluene (40 mL) and pyridine (20 mL) were added to a mixture of telechelic hydroxylated poly[(*R*)-3-hydroxyoctanoate] (PHO-diol) (1.205 g, 0.502 mmol, M_n = 2400, M_p = 2100), telechelic hydroxylated poly[(*R*)-3-hydroxybutyrate] (PHB-diol) (1.01 g, 0.388 mmol, M_n = 2600, M_p = 3200), and terephthaloyl chloride (0.164 g, 0.808 mmol) in a 250 mL flask under a nitrogen atmosphere. The stirred mixture was heated progressively to 80 °C to dissolve the reactants and then to 105 °C for polycondensation. The reaction was stopped after 12 h by cooling, and the solvent was evaporated. The product was treated four times with chloroform/water 1:4 (v/v), and the organic phase was separated and then washed vigorously three times with aqueous HCl (0.1 M) to remove pyridine and the possible unreacted terephthaloyl chloride. The collected organic phase was dried over Na_2SO_4 and filtered, and the solvent was evaporated. Drying under high vacuum at 80 °C gave 2.01 g (86%) of the block copolyester PHOHBT with an M_p of 7200 (measured by GPC).

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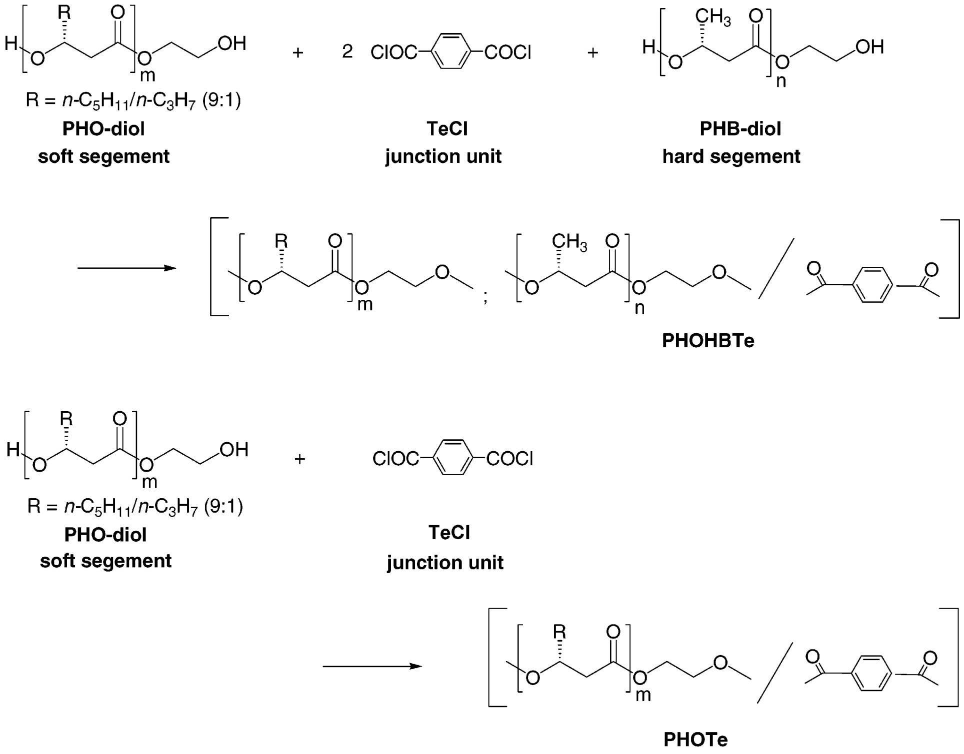
Scheme 1



Synthesis of Interchange Polyester PHOTe. Similar to the procedure described for PHOHBTe, reaction of PHO-diol (1.023 g, 0.426 mmol, $M_n = 2400$, $M_p = 2100$) and terephthaloyl chloride (0.102 g, 0.502 mmol) in a mixture of toluene (40 mL), chloroform (5.0 mL), and pyridine (5.0 mL) at 105 °C for 30 h afforded 0.90 g (81%) of PHOTe with an M_p of 7100 (measured by GPC).

Characterization Techniques. ^1H and ^{13}C NMR spectra were measured on a Bruker DRX-300 (300 MHz) at 293 K in $CDCl_3$. COSY (^1H, ^{13}C) and COSY (^1H, ^1H) were measured on a Bruker DRX-400 (400 MHz) at 300 K in $CDCl_3$. Chemical shifts are given in ppm relative to tetramethylsilane. IR spectra (film) were recorded on a Bruker Vector 22 spectrometer at room temperature. The molecular weight distribution was determined by gel permeation chromatography (GPC) in THF at room temperature with a Knauer chromatograph equipped with a differential refractive index detector with two PLGel mixed 5 μm columns (7.5 mm × 600 mm) at 85 bar and at 45 °C. M_p was estimated from the retention volume based on polystyrene standards. T_m and T_g were obtained by differential scanning calorimetry (DSC) with a Mettler-DSC 30 instrument equipped with Me-70329 cooler and a Tc15/TA controller. The samples in a 40 μL aluminum carrier were heated in the first scan from −100 to 200 °C with a heating rate of 10 °C/min, cooled from 200 to −100 °C at a cooling rate of −10 °C/min, and then heated for the second scan.

Results and Discussion

Poly[(*R*)-3-hydroxyoctanoate] (PHO) is the most prominent representative of mcl-PHAs, and it can be produced in large amounts. Transesterification of PHO with ethylene glycol afforded enantiopure telechelic PHO-diol with a M_n of 2400 (VPO), a M_p of 2100 (GPC), and a T_g of −56 °C in excellent yield.[18] This readily available compound was selected as the soft segment for the preparation of block copolyesters. On the other hand, telechelic diol prepared from poly[(*R*)-3-hydroxybutyrate] (PHB-diol)[20] with a T_m of 149 °C, a M_n of 2600 (VPO), and a M_p of 3200 (GPC) was chosen as the hard segment. Terephthaloyl chloride (TeCl) was used as junction unit. In principle, the ratio of the soft segment, hard segment, and the junction unit can be controlled to prepare the block co-polyesters with desired properties. To demonstrate the concept, PHO-diol, PHB-diol, and TeCl were used in a molar ratio of 1.3:1:2.1 to prepare the co-polyester PHOHBTe (Scheme 1). For a comparison, interchange polyester PHOTe containing no PHB block was also synthesized from PHO-diol and TeCl in a molar ratio of 1:1.2.

New polyesters were formed by the reaction between the COCl groups of TeCl and the OH groups of the telechelic diols. Since water can stop the polymerization by reacting with TeCl to give the corresponding acid, the reaction was carried out under anhydrous conditions and under a nitrogen atmosphere. PHO-diol and PHB-diol were at first dried by azeotropic distillation with 1,2-dichloroethane and then reacted with TeCl in a mixture of toluene and pyridine at 105 °C for 12 h. The solvent was removed by evaporation, the residue was treated with water to destroy the possible unreacted TeCl, and the product was extracted into $CHCl_3$. Subsequent treatment of organic phase with 0.1 M HCl removed the trace amount of pyridine. Drying under high vacuum at 80 °C afforded the block copolyester PHOHBTe in 86% yield. A molecular weight M_p of 7200 was established by gel permeation chromatography (GPC), shown in Figure 1. Similarly, PHOTe containing only the soft PHO block was prepared in 81% yield by reaction of PHO-diol with TeCl in a molar ratio of 1:1.2 at 105 °C for 30 h. The resulting material has a M_p of 7100 (GPC), which is similar to that of PHOHBTe (Figure 1).

In the IR spectra of PHOBOTe, the two absorption bands of the OH groups of the starting materials PHO-diol and PHB-diol at 3530−3350 cm^{-1} decreased significantly, indicating the successful polymerization. The ester functions were confirmed by the strong absorption at 1735 cm^{-1}.

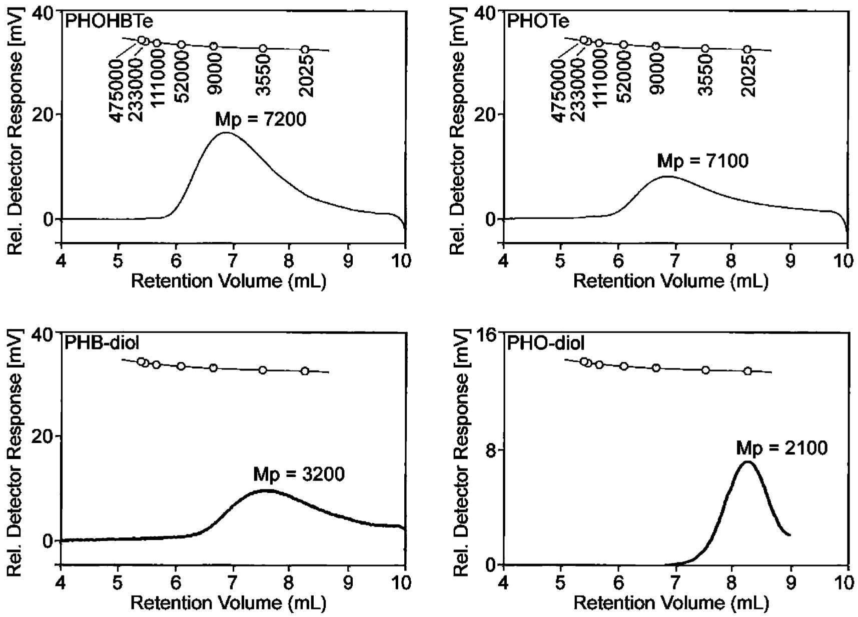


Figure 1. GPC chromatograms of the block copolyester PHOHBTe, the interchange polyester PHOTe, the hard segment PHB-diol, and the soft segment PHO-diol.

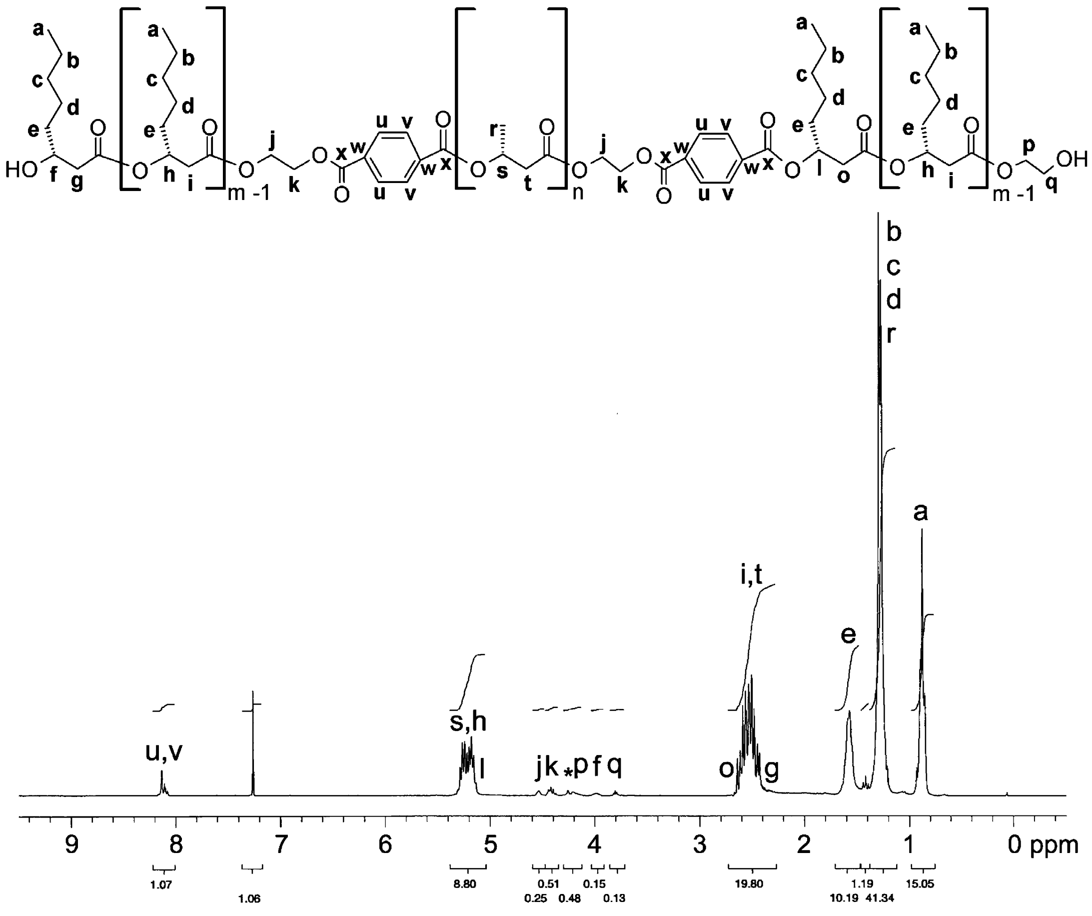


Figure 2. ^{1}H-NMR spectrum (300 MHz) of the block copolyester PHOHBTe at 293 K in CDCl$_3$. * $-OCH_2CH_2O-$ of bis substituted ethylene glycol in PHO-diol block.

The structure of PHOHBTe was confirmed by NMR analyses. The ^{1}H- and COSY (^{1}H, ^{13}C)-NMR spectra are given in Figures 2 and 3, respectively. On the basis of the COSY (^{1}H, ^{1}H)- and COSY (^{1}H, ^{13}C)-NMR spectra and comparison with the ^{1}H-NMR spectrum of PHO-diol, the chemical shifts of all protons of PHOHBTe were assigned as shown in Figure 2. The assignment of the ^{13}C chemical shifts is also possible, and the result is summarized in Table 1. Although the PHO block contains C8 and C6 monomer in a ratio of 90:10, there was no significant difference between the C8 and C6 monomers in the ^{1}H-NMR spectrum, and the C6 monomers gave only several additional weak signals in the ^{13}C-NMR spectrum. For simplicity, only the assignment

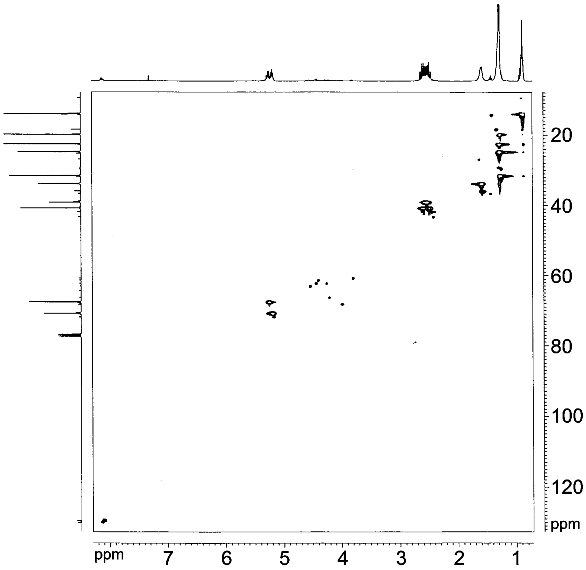


Figure 3. COSY (^{1}H, ^{13}C)-NMR spectrum (400 MHz) of the block copolyester PHOHBTe at 300 K in $CDCl_3$ (shown only 10−130 ppm from ^{13}C-NMR).

for the C8 monomer of the PHO block was given in this work.

PHO-diol with M_n of 2400 contains 16.8 HO monomer units (m) on average, while PHB-diol with M_n of 2600 has the average number of HB monomer units (n) of 29.5. In the ^{1}H-NMR spectrum of PHOHBTe, the intensity of methyl group proton **a** of the PHO block is 15.05; thus, the intensity of proton **i**, **o**, and **g** of the same block should be 15.05 × $^2/_3$ = 10.03. While the total integration of proton **i**, **o**, **g** and **t** is 19.80, the intensity of proton **t** from the PHB block should be 19.80 − 10.03 = 9.77. The ratio of the PHO and PHB block in PHOHBTe can be therefore deduced as about 2:1 (10.03/16.8:9.77/29.5). The aromatic proton **u** and **v** of the Te part had an integration of 1.07, which suggested that the ratio of Te junction unit and PHO block is about 1:1 (1.07/4:15.05/3/16.8). Although M_n of PHOHBTe was not determined, the M_p value of 7200 for PHOHB suggests that on average it contains 2 PHO (M_p of 2100) blocks, 1 PHB (M_p of 3200) block, and 2 Te junction units. The major terminating groups are the primary and secondary alcohols, which is confirmed by the signals of proton **f**, **g** and **p**, **q**.

Table 1. Assignment of Chemical Shifts of PHOHBTe in the ^{13}C NMR Spectrum

position	δ (^{13}C)	position	δ (^{13}C)
a	14.0	**l**	71.9
b	22.5	**o**	41.8
c	24.7	**p**	66.3
d	31.5	**q**	60.8
e	33.8	**r**	19.8
f	68.2	**s**	67.6
g	43.3	**t**	40.8
h	70.9	**u, v**	129.5, 129.7, 130.0
i	39.1	**w**	133.5, 133.8, 134.6
j	63.1	**x**	165.4, 165.8, 172.0, 172.4
k	62.3	C=O (HB, HO)	169.2, 169.4

Similarly, the structure of PHOTe was also confirmed by ^{1}H, ^{13}C, COSY (^{1}H, ^{1}H), and COSY (^{1}H, ^{13}C)-NMR spectra. The chemical shift assignments for the ^{1}H-NMR spectrum are given in Figure 4. Comparison of the intensities of proton **a** of PHO and proton **u** and **v** of

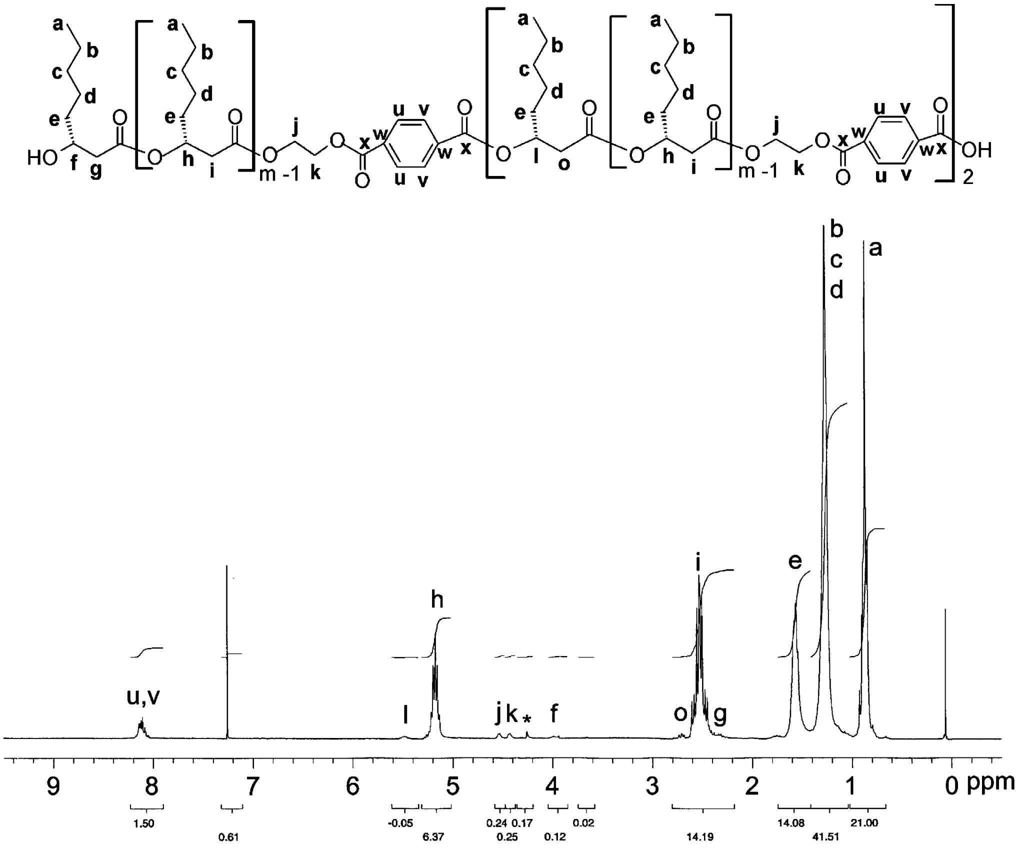


Figure 4. ^{1}H-NMR spectrum (300 MHz) of the interchange polyester PHOTe at 293 K in $CDCl_3$. (*) $-OCH_2CH_2O-$ of bis-substituted ethylene glycol in PHO-diol block.

Table 2. Physical Properties of PHOHBTe, PHOTe, PHO, PHB, P(3HB-*co*-3HA), and Polypropylene (PP)

properties	PHOHBTe	PHOTe	PHO[a]	PHB[b]	P(3HB-*co*-3HA)[c]	PP[d]
M_w (GPC)			66000	539000	1391500	700000
M_n (GPC)			23600	154000	605000	60000
M_p (GPC)	7200	7100				
M_w/M_n (GPC)	1.6	2.1	2.8	3.5	2.3	5−12
T_g (°C, DSC)	−41	−36	−30	4	−8	−10
T_m (°C, DSC)	129, 140		61	180	133, 146	176

[a] Data from ref 19. [b] Data from ref 22. [c] Biosynthetic copolyester consisting of 94 mol % 3HB and 6 mol % 3HA; data from ref 16. [d] Data from ref 1.

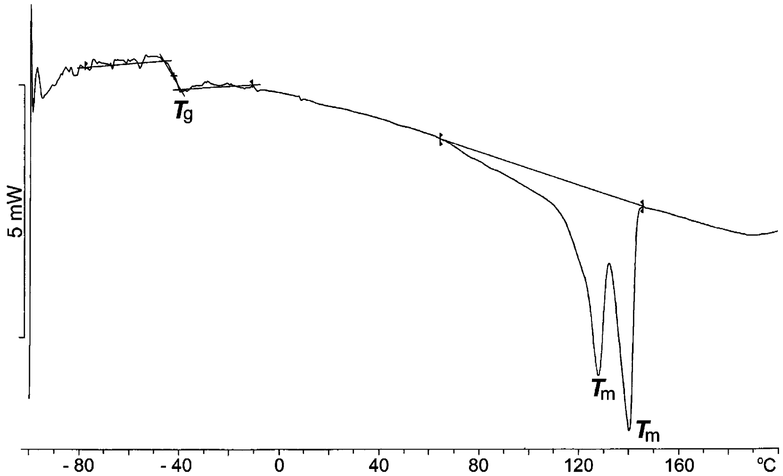


Figure 5. DSC spectrum of the block copolyester PHOHBTe.

the Te part revealed a 1:1 ratio of PHO and Te. On the basis of M_p of 7100 for PHOTe, it can be concluded that on average 3 PHO (M_p of 2100) blocks and 3 Te junction units are incorporated in the interchange polyester PHOTe.

The physical properties of the new polymers were characterized by DSC and are listed in Table 2. The interchange polyester PHOTe with only the soft PHO as polyester backbone linked with an aromatic junction unit did not result in a hard polymer: the new polymer is soft-sticky with no T_m and a T_g of −36 °C. On the other hand, the co-polyester PHOHBTe containing PHB and PHO-blocks as hard and soft segments, respectively, showed good thermoplastic properties with a T_g of −41 °C and T_m of 128 and 140 °C (Figure 5). This T_g is probably for the PHO segment, and the T_g value of PHB segment was not observed. A second heating for DSC measurement revealed a T_c of 60 °C. Although the molecular weight is not very high, PHOHBTe represents the first example of block copolyester containing the soft PHO and hard PHB blocks. Comparing with the random copolyester P(3HB-*co*-3HA) consisting of 94 mol % HB and 6 mol % HA,[16] PHOHBTe has similar T_m but much lower T_g. The molecular weight of the block polymer-could be in principle further increased, for instance, by performing the reaction under argon atmospheres and/or by using other junction units. The existence of the PHB block in such copolyesters is proven to be essential for increasing the melting and mechanic properties. The physical properties of new block copolyester could be designed and achieved by changing the ratio of PHO and PHB blocks.

Conclusions

For the first time, co-polyesters containing biodegradable and biocompatible PHO and PHB blocks have been synthesized by use of PHO-diol and PHB-diol as soft and hard segments, respectively. The model polymer PHOHBTe shows good thermoplastic properties, and the physical properties of the block copolyester can be further optimized by incorporation of the PHO and PHB blocks in an appropriate ratio.

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Supporting Information Available: ^{13}C-, COSY (^{1}H, ^{1}H)-, and COSY (^{1}H, ^{13}C)-NMR and IR spectra of the block copolyester PHOHBTe; ^{13}C-, COSY (^{1}H, ^{1}H)-, and COSY (^{1}H, ^{13}C)-NMR spectra of the interchange polyester PHOTe. This material is available free of charge via the Internet at http://pubs.acs.org.

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