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Synthesis and Characterization of New Biodegradable Amphiphilic Poly(ethylene oxide)-*b*-poly[(*R*)-3-hydroxy butyrate]-*b*-poly(ethylene oxide) Triblock Copolymers

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ABSTRACT: New biodegradable amphiphilic ABA triblock copolymers consisting of poly(ethylene oxide) (PEO) as the hydrophilic block and poly[(*R*)-3-hydroxy butyrate] (PHB) as the hydrophobic block were synthesized by coupling two chains of methoxy-PEO-monocarboxylic acid with a low molecular weight telechelic hydroxylated PHB (PHB-diol) chain in the middle. The PHB-diol was prepared from high molecular weight natural source PHB by transesterification reaction with diethylene glycol. The target triblock copolymers were isolated and purified from the reaction mixtures through repeated precipitation and fractionation. The structures and molecular characteristics of the PEO−PHB−PEO triblock copolymers were studied by GPC, ^{1}H NMR, and FT-IR. All of the triblock copolymers had unimodal peaks in the GPC chromatographs. The chain architecture of the triblock copolymers was confirmed by the ^{1}H NMR spectra. A combination of GPC and ^{1}H NMR analysis determined the lengths of the PEO and PHB blocks of the copolymers. The thermal properties, phase separation, and crystalline characteristics of the copolymers were studied using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and wide-angle X-ray diffraction (XRD). TGA analysis showed that the triblock copolymers undergo thermal degradation in two separate steps for the PHB and PEO blocks, from which the PHB contents were calculated and compared with those determined from GPC and ^{1}H NMR. The TGA results also showed that the triblock copolymers have better thermal stability than their respective precursors. Both DSC and XRD analysis showed that separate crystalline phases are formed by PEO and PHB blocks in the copolymers, except for those with a very short PHB block length. The crystallinity of PHB block in the copolymers increases as compared with the pure PHB precursor, presumably because of the presence of the soft PEO block. In contrast, the crystallinity of the PEO block in the copolymers decreases as compared with the PEO precursor because of the presence of the hard PHB block, which restricts the crystallization of the PEO blocks.

Introduction

Amphiphilic block copolymers have attracted special attention in both fundamental and applied research because of their unique chain architecture and physical properties.[1,2] For example, they have been extensively studied as building blocks in supramolecular chemistry for highly ordered self-assembled structures.[1−5] With interesting association and phase behavior in aqueous environment, they also have attracted great interest in biomaterials applications. From micelle formation to thermally induced gelation, these amphiphilic block copolymers find interesting applications in drug delivery and tissue engineering.[6,7]

Poly(ethylene oxide) (PEO), as a hydrophilic and biocompatible polyether, is widely used in biomedical research and application.[8] Amphiphilic ABA triblock copolymers consisting of PEO as the hydrophilic segments are particularly popular. As a typical example, commercially available poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO, Pluronics) triblock copolymers have been studied extensively in terms of their phase behavior and potential applications for drug delivery.[9,10] Recently, with biodegradability as a desirable feature, more attention has been focused on incorporating biodegradable segments as the hydrophobic block together with the hydrophilic PEO block. Therefore, amphiphilic triblock copolymers consisting of PEO and biodegradable polyesters such as poly(L-lactic acid) (PLLA), poly(glycolic acid) (PGA), or their copolyesters have been synthesized with fascinating self-association, gelation, and nanoscaled ordering behavior.[11−13]

Poly[(*R*)-3-hydroxy butyrate] (PHB) and related poly[(*R*)-3-hydroxy alkanoates] (PHA) are a class of natural biopolyesters produced by many microorganisms as intracellular carbon and energy storage material.[14] A trace of low-molecular-weight PHB was found in a variety of prokaryotic and eukaryotic cells,[15−17] or even in human blood plasma,[18] forming channels in cell transmembranes, which plays an important role in the physiological processes. Being biocompatible and biodegradable, PHB is also attractive for various biomedical applications. Therefore, much attention has been focused on studies of the fine structures of natural PHB as well as molecular design by using both natural PHB and its synthetic analogues.[19−30] Seebach's group has synthesized oligomers of (*R*)-3-hydroxybutyric acid (OHB) with well-defined chain lengths, and studied the OHB-mediated ion transport through phospholipid bilayers, for understanding of the role of PHB in physiological

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processes.[19,20] We studied the fine structures and conformational behavior of OHB with various end groups as model compounds of the natural PHB.[21,22] For molecular design of special copolymers, telechelic hydroxylated PHB (PHB-diol) with low molecular weights was synthesized by transesterification from the natural isotactic PHB.[23] Usually, ring-opening polymerization of β-butyrolactone results in atactic PHB segments with good solubility but lacking crystallinity. Atactic PHB-diol containing primary hydroxy ends was synthesized by this method, and its structure was verified by electrospray ionization mass spectroscopy.[24] However, a novel facile synthesis of PHB exhibiting almost identical structure with natural isotactic PHB based on regioselective ring-opening polymerization of (S)-β-butyrolactone was reported.[25]

Block copolymers of PHB with other polyesters or polyurethanes have been synthesized for modification of the mechanical properties of PHB.[26−28] Recently, amphiphilic diblock copolymers were synthesized by catalyzed transesterification in the melt from bacterial PHB and monomethoxy PEO (M-PEO) in a one-step process.[29] A biochemical route to PHA−PEO diblock copolymers by addition of PEO (M_n = 200 or 400) to fermentation was also reported recently.[30] The purpose of the addition of PEO is to regulate the molar mass and end group structure in the PHA produced by cells, and the PEO content remains below 0.5 wt % in the PHA−PEO copolymers, which cannot really function as a block copolymer. To our knowledge, there have been no reports on success at synthesizing amphiphilic triblock copolymers containing PHB as the middle block and PEO. Disparity in hydrophobicity between the blocks and the crystallinity of the hydrophobic segments are two important parameters that dictate the self-assembly and phase behavior of amphiphilic block copolymers. A new ABA triblock copolymer of PEO with PHB as the middle block would have novel properties because the isotactic PHB is highly crystalline and hydrophobic, significantly more so than PLLA and PGA. Moreover, PHB has lower in vivo degradation rate than PLLA and many other biopolyesters.[31] Therefore, the possibly lower biodegradation rate of such PEO−PHB−PEO triblock copolymers would be advantageous in biomedical or environmental applications where higher stability is desired.

Herein, we have successfully synthesized the new PEO−PHB−PEO triblock copolymers starting from high molecular weight natural PHB produced via biosynthesis. The high-molecular-weight natural source PHB was first converted into low-molecular-weight telechelic hydroxylated PHB (PHB-diol). The triblock copolymers were synthesized by coupling the PHB-diol with two chains of methoxy-PEO-monocarboxylic acid (M-PEO-A). The structures and molecular characteristics of the PEO−PHB−PEO triblock copolymers were studied by GPC,^{1}H NMR, and FT-IR. The thermal properties, phase separation, and crystallization behavior of the copolymers were studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and wide-angle X-ray diffraction (XRD).

Experimental Section

Materials. Natural source poly[(R)-3-hydroxy butyrate] (PHB) was purchased from Aldrich. The PHB sample was purified by dissolving in chloroform followed by filtration and precipitation in petroleum ether before use. The M_n and M_w of the purified PHB are 8.7×10^4 and 2.3×10^5, respectively. Methoxypoly(ethylene oxide) monopropionic acid (M-PEO-A) with molecular weight of ca. 5000 was purchased from Shearwater Polymers, Inc. Its M_n and M_w were found to be 4740 and 4880, respectively. Methoxypoly(ethylene oxide) (M-PEO) with molecular weight of ca. 2000 was purchased from Sigma. Its M_n and M_w were found to be 1820 and 1870, respectively. Bis(2-methoxyethyl) ether (Diglyme, 99%), ethylene glycol (99%), dibutyltin dilaurate (95%), 1,3-N,N'-dicyclohexylcarbodiimide (DCC, 99%), 4-(dimethylamino)pyridine (DMAP, 99%), succinic anhydride (97%), and triethylamine (99%) were obtained from Aldrich. Diglyme was dried with molecular sieve, and methylene chloride was distilled from CaH_2 before use.

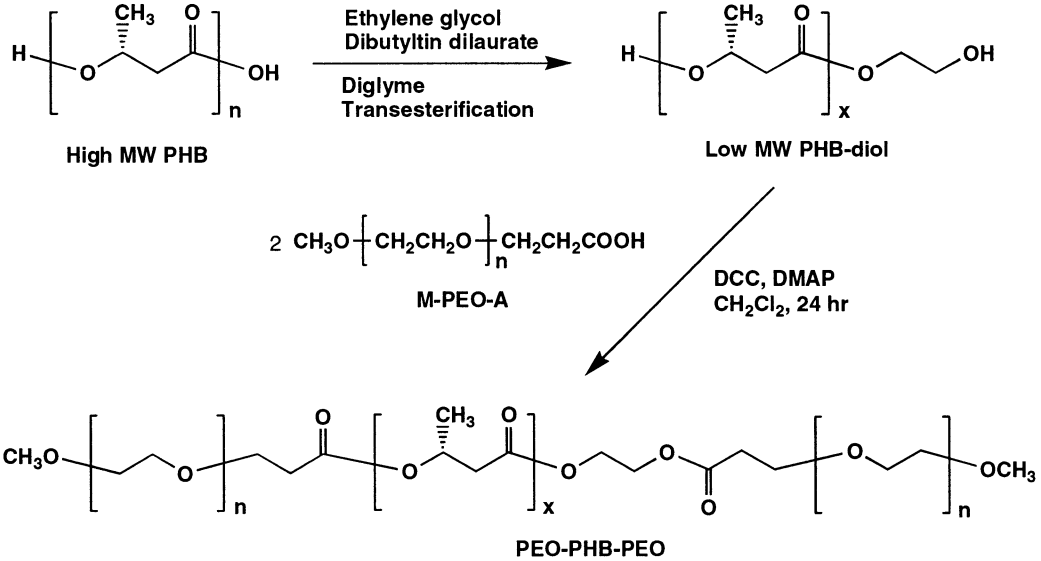
Telechelic hydroxylated PHB (PHB-diol) prepolymers with various molecular weights were prepared by transesterification from the natural PHB and diethylene glycol with dibutyltin dilaurate as catalyst in diglyme as reported previously (yield, 80%).[23] M-PEO-monocarboxylic acid (M-PEO-A) prepolymers with M_n of 1820 were prepared by reaction of M-PEO with succinic anhydride in the presence of DMAP and triethylamine in 1,4-dioxane as reported previously.[32]

Synthesis of the PEO−PHB−PEO Triblock Copolymers. As one typical example, PHB-diol (0.38 g, 1.2×10^{-4} mol, $M_n = 3220$), M-PEO-A (1.42 g, 3.0×10^{-4} mol, $M_n = 4740$), and DMAP (12 mg, 9.8×10^{-5} mol) were dried in a 50 mL two-neck flask under vacuum at 60 °C (oil bath) overnight. Anhydrous methylene chloride (25−30 mL) was added to the flask, and then was removed by distillation (oil bath, 75 °C), to remove any trace water in the system. When the flask cooled, DCC (0.098 g, 4.7×10^{-4} mol) dissolved in 4 mL of anhydrous methylene chloride was added, and the solution was stirred overnight at room temperature under nitrogen. Precipitated dicyclohexylurea (DCU) was removed by filtration. The polymer was precipitated from diethyl ether (two times). The desired triblock copolymer product, redissolved in methanol or chloroform, was further purified by fractionation. Yield: 0.75 g, 56%. GPC (THF): M_n = 12 720, M_w = 13 770, M_w/M_n = 1.08. T_m = 54 °C (for PEO block) and 140 °C (for PHB block). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (m, mechine H of PHB block), 4.32 (s, $-COOCH_2CH_2COO-$), 3.68 (s, $-CH_2OCH_2-$ of PEO block), 3.42 (s, $-OCH_3$ end group), 2.48−2.67 (m, methylene H of PHB block), 1.31 (d, methyl H of PHB block). IR (KBr): 2886, 1723, 1456, 1380, 1280, 1111, 1061, 962, 842, 516 cm^{-1}.

Molecular Characterization. Gel permeation chromatography (GPC) analysis was carried out with a Shimadzu SCL-10A and LC-8A system equipped with two Phenogel 5μ 50 and 1000 Å columns (size: 300 × 4.6 mm) in series and a Shimadzu RID-10A refractive index detector. THF was used as eluent at a flow rate of 0.30 mL/min at 40 °C. Monodispersed poly(ethylene glycol) standards were used to obtain a calibration curve. The ^{1}H NMR spectra were recorded on a Bruker AV-400 NMR spectrometer at 400 MHz at room temperature. The ^{1}H NMR measurements were carried out with an acquisition time of 3.2 s, a pulse repetition time of 2.0 s, a 30° pulse width, 5208 Hz spectral width, and 32K data points. Chemical shift was referred to the solvent peaks (δ = 7.3 ppm for $CHCl_3$). Fourier transform infrared (FT-IR) spectra were recorded on a Bio-Rad 165 FT-IR spectrophotometer; 64 scans were signal-averaged with a resolution of 2 cm^{-1} at room temperature. Samples were prepared by dispersing the polymers in KBr and compressing the mixtures to a disk.

Thermal Analysis. Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments 2920 differential scanning calorimeter equipped with an autocool accessory and calibrated using indium. The following protocol was used for each sample: heating from room temperature to 200 °C at 20 °C min^{-1}, holding at 200 °C for 2 min, cooling from 200 to −30 °C at 5 °C min^{-1}, and finally reheating from −30 to 200 °C at 5 °C min^{-1}. Data were collected during the second heating run. Transition temperatures were taken as peak maxima. Thermogravimetric analyses (TGA) were made using a TA Instruments SDT 2960. Samples were heated at 20 °C min^{-1} from room temperature to 800 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL min^{-1}).

Scheme 1. Synthesis of the PHB-diol Precursors and the PEO−PHB−PEO Triblock Copolymers



Wide-Angle X-ray Diffraction. X-ray diffraction (XRD) measurements were carried out on a Simens D5005 diffractometer using Ni-filtered Cu Kα (1.540 Å) radiation (40 kV, 40 mA). Film samples were mounted on a sample holder and scanned in 0.01° steps from 5° to 35° (in 2θ) with 1 s per step.

Results and Discussion

Synthesis and Molecular Characterization. The procedures for synthesis of the PEO−PHB−PEO triblock copolymers are presented in Scheme 1. We first converted high-molecular-weight natural source PHB into telechelic hydroxyl-terminated PHB (PHB-diol) with lower molecular weights by transesterification with ethylene glycol.[23] The transesterification reaction was allowed to proceed for a few hours to overnight to produce PHB-diol with average molecular weights ranging from a few hundred to a few thousand as determined by GPC. The PHB-diol was then allowed to react with methoxy-PEO-monocarboxylic acid (M-PEO-A, M_n 1820 or 4740) using DCC to give the PEO−PHB−PEO triblock copolymers. Since the reaction is moisture-sensitive, it was carried out in dried methylene chloride under a nitrogen atmosphere. The target triblock copolymers were isolated and purified from the reaction mixture by repeated precipitation and fractionation.

GPC analysis was performed to determine the molecular weights and molecular weight distributions of the triblock copolymers. GPC chromatographs of all purified triblock copolymers showed peaks that are unimodal. Figure 1 shows a typical GPC chromatogram for one of the PEO−PHB−PEO triblock copolymers together with the corresponding prepolymers. The molecular weight of the PEO−PHB−PEO triblock copolymer is higher than its PEO and PHB precursors, corresponding to the ABA triblock structure. The polydispersity of the final copolymer is lower than that of the PHB-diol, mostly likely due to fractionation, which removes the copolymer with shorter PHB segments that has higher solubility.

The chemical structure of the triblock copolymers was confirmed by ^{1}H NMR spectroscopy, which was also used to determine the lengths of the middle PHB segments and the composition of the copolymers. Figure 2 shows the ^{1}H NMR spectra of a PEO−PHB−PEO triblock copolymer and its starting prepolymers. Since the two M-PEG-A prepolymers used in this work are almost monodispered (M_w/M_n = 1.03), the molecular weights of PEO blocks in the copolymers can be considered identical to their M-PEO-A prepolymers. Therefore, the molecular weight of the PHB block in the copolymers can be determined from the ratio between integrals of peaks for PHB and PEO segments. The ^{1}H NMR spectra also provide strong evidence for quantitative reaction of the PHB-diol. In Figure 2b, the protons of the PHB hydroxy end unit clearly appear at 1.26 ppm (doublet) for *c′* and 4.25 ppm (multiplet) for *b′*,[21,22] while the ethylene glycol end group can be seen at 3.84 ppm (triplet) for *d* and 4.26 ppm (triplet) for *e*.[23] In Figure 2c, all peaks for the PHB hydroxy end unit disappear, and those of ethylene glycol end group become a single peak at 4.32 ppm, confirming the complete conjugation of M-PEO-A to PHB-diol.

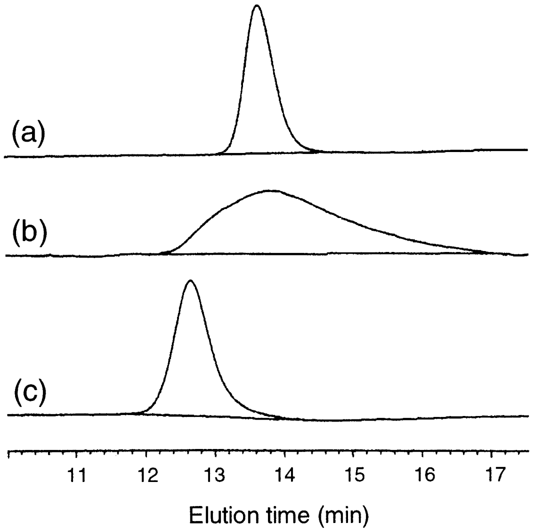


Figure 1. GPC traces of the PEO−PHB−PEO triblock copolymer and its PEO and PHB precursors: (a) M-PEO-A (M_n = 4740, M_w/M_n = 1.03); (b) PHB-diol (M_n = 3220, M_w/M_n = 1.46); and (c) EHE(50-38-50) (M_n = 12 720, M_w/M_n = 1.08).

Table 1 presents the molecular weights, molecular weight distributions, and compositions (block lengths and PHB contents in weight) of all triblock copolymers synthesized in this work. All copolymers showed rela-

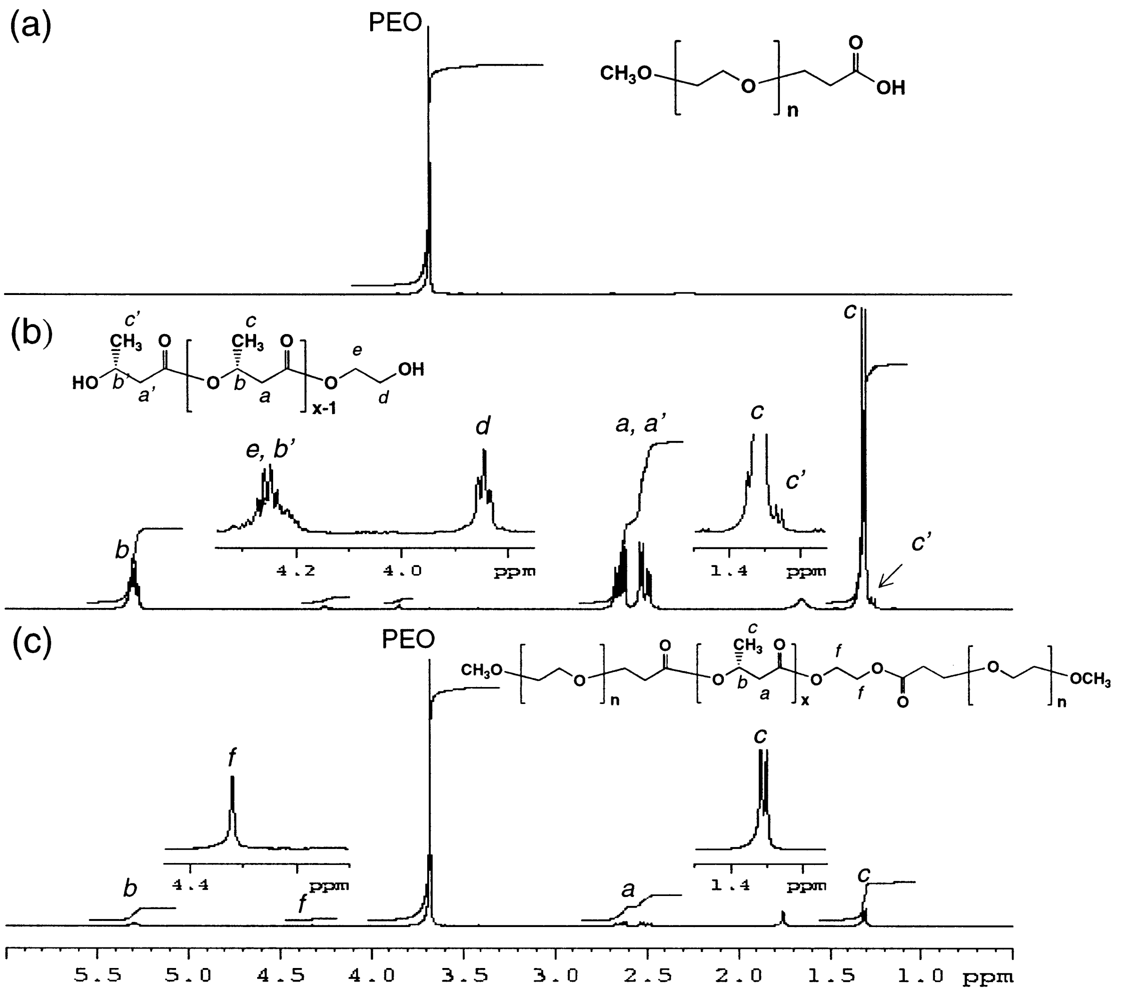


Figure 2. The 400 MHz ^{1}H NMR spectra for (a) M-PEO-A (M_n 4740), (b) PHB-diol (M_n 3220), and (c) PEO−PHB−PEO triblock copolymer EHE(50-38-50) in $CDCl_3$ at room temperature.

Table 1. Molecular Characteristics of the PEO−PHB−PEO Triblock Copolymers

				block length (M_n)		PHB content (wt %)	
copolymer[a]	M_n[b]	M_w[b]	M_w/M_n[b]	PEO[b]	PHB[c]	NMR[c]	TGA[d]
EHE(20-05-20)	4500	4730	1.05	1820	470	11.4	12.6
EHE(20-39-20)	7290	8000	1.10	1820	3910	51.8	52.0
EHE(20-52-20)	8120	9260	1.14	1820	5230	59.0	58.3
EHE(50-08-50)	10390	11200	1.08	4740	780	7.6	8.4
EHE(50-38-50)	12720	13770	1.08	4740	3820	28.7	29.7
EHE(50-55-50)	13390	16250	1.21	4740	5490	36.7	38.2

[a] The PEO−PHB−PEO triblock copolymers are denoted EHE, and the numbers in brackets show the indicative molecular weight of respective block in hundred g/mol. [b] Determined by GPC. [c] Determined by combination of ^{1}H NMR and GPC results. [d] Calculated from TGA results.

tively narrow molecular weight distributions. Two series of triblock copolymers were synthesized using M-PEO-A of M_n 1820 or 4740. The middle PHB block length ranges from a few hundred to more than 5000, corresponding to 8 to 59 wt % in the copolymers. Triblock copolymers with lower PHB contents such as EHE-(20-05-20), EHE(50-08-50), and EHE(50-38-50) are water-soluble. Our preliminary studies showed that they form micelles in an aqueous environment at very low polymer concentrations (results will be reported elsewhere).

The FT-IR spectra of EHE(20-39-20) and its starting PEO and PHB precursors are shown in Figure 3. All of the characteristic absorptions for PHB and PEO segments appear in the spectrum of the triblock copolymer. The carbonyl stretch occurs at 1723 cm^{-1} for the copolymer and PHB precursor. The ether stretch occurs at 1102 cm^{-1} for the copolymer and PEO precursor. The bands at 963 and 843 cm^{-1} are the characteristic of the crystalline phase of PEO.[33] The two peaks appear in the spectrum of the copolymer, and their intensities are associated with the content of PEO block and its crystallinity. The results agree well with those from DSC and XRD, which will be discussed in the following sections.

Thermal Stability. The thermal stability of the triblock copolymers was evaluated using thermogravimetric analysis (TGA). Figure 4 shows the weight loss curves for a triblock copolymer compared with its PEO and PHB precursors. The PEO−PHB−PEO triblock copolymers undergo stepwise thermal degradation. The PHB block starts degrading first at about 260 °C, followed by the PEO block at about 350 °C. The PEO

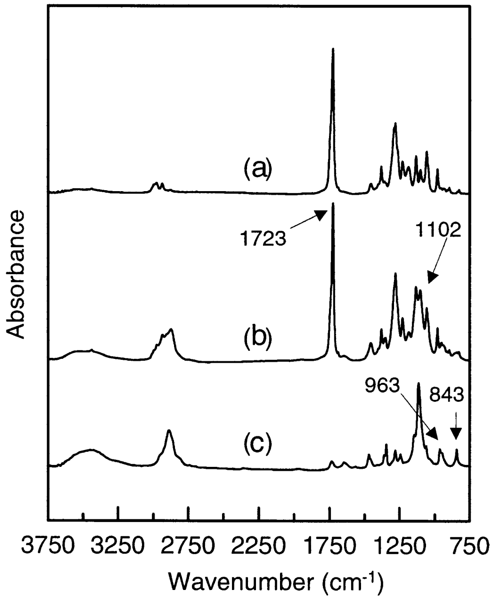


Figure 3. FT-IR spectra of (a) PHB-diol (M_n 3220), (b) PEO−PHB−PEO triblock copolymer EHE(20-39-20), and (c) M-PEG-A (M_n 1840).

block starts degradation after the PHB block has completed its degradation at 310−320 °C. Therefore, the compositions of the triblock copolymers can be calculated from the two-step degradation. The PHB contents estimated from TGA results are listed in Table 1, which are similar to those obtained from ^{1}H NMR. We use the temperature at which 10% of mass loss has occurred for each block of the copolymers as the decomposition temperature[34] (T_d) to quantitatively evaluate the thermal stability, and the results for all triblock copolymers are listed in Table 2. The results show that the triblock copolymers have better thermal stability than their respective precursors.

Solid-State Behavior. Differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (XRD) studies were carried out to determine the microphase separation and crystallization behavior of the PEO and PHB blocks in the copolymers. Figures 5 and 6 show the DSC thermograms for the PEO and PHB precursors and the PEO−PHB−PEO triblock copolymers with different compositions. In addition, numerical values corresponding to the thermal transitions and the crystallinity of each block are presented in Table 2. Both PEO and PHB are crystalline polymers.[14,33] For copolymers EHE(20-05-20) and EHE(50-08-50) with short PHB block, the PHB melting transition peak is not observed, indicating that the PHB crystalline phase is not formed. For these two copolymers, the PHB crystalline phase could not be formed even after annealing at 110 °C for 10 h. For the copolymers with longer PHB block, the melting transition temperature (T_m) of PHB block decreases with decrease in PHB block length. The melting enthalpy and the crystallinity of PHB block significantly increase in the copolymers as compared with the pure PHB-diol, presumably being caused by the existence of the soft PEO block.

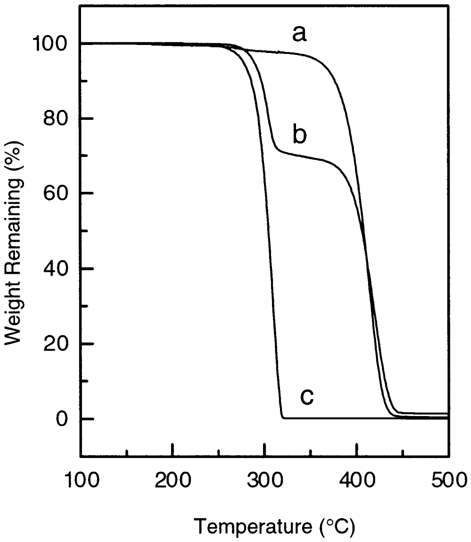


Figure 4. TGA curves obtained at a heating rate of 20 °C/min under a nitrogen atmosphere for (a) M-PEO-A (M_n 4740), (b) triblock copolymer EHE(50-38-50), and (c) PHB-diol (M_n 3220).

In contrast, PEO blocks in all triblock copolymers have lower melting enthalpy and lower crystallinity as compared with the those of pure PEO precursors. The melting temperatures, melting enthalpies, and crystallinity of PEO block all decrease with increase in PHB block length or the content of PHB in the copolymers. These may be caused by the hard PHB block, which restricted the crystallization of PEO blocks in the copolymers to a certain extent. The melting temperature

Table 2. Transition Temperatures, Corresponding Enthalpies, Crystallinity for Polymer Samples, and Their Decomposition Temperatures

	T_m (°C)[b]		ΔH_m (J/g)[c]		X_c[d]		T_d (°C)[e]	
polymer sample	PEO	PHB	PEO	PHB	PEO	PHB	PHB	PEO
M-PEO-A (M_n 1820)	53.2		149.6		73.0			372.2
M-PEO-A (M_n 4740)	58.8		165.5		80.7			379.4
PHB-diol (M_n 3220)		155.2		78.2		53.3	269.1	
EHE(20-05-20)[a]	52.0		135.4		66.0		280.6	383.3
EHE(20-39-20)[a]	25.4	142.3	69.1	92.2	33.7	62.8	279.8	382.9
EHE(20-52-20)[a]	23.3	153.6	58.3	97.8	28.4	66.7	278.2	378.0
EHE(50-08-50)[a]	57.7		148.7		72.5		284.8	384.7
EHE(50-38-50)[a]	54.1	140.2	119.4	97.8	58.2	66.7	283.8	391.0
EHE(50-55-50)[a]	50.4	153.2	111.0	107.8	54.1	73.6	286.0	387.8

[a] The PEO−PHB−PEO triblock copolymers are denoted EHE, and the numbers in brackets show the indicative molecular weight of respective block in hundred g/mol. [b] Melting point determined by DSC second heating-up run. For PHB-diol having multipeak endothem due to melting−recrystallization, the T_m value for the second peak is given. [c] Enthalpy change during melting determined by DSC second heating-up run. $\Delta H_m = \Delta H_i/w_i$, where ΔH_i is the area of the endothermic peak for PEO or PHB block read from Figures 5 and 6, and w_i is the weight fraction of the corresponding block. [d] Crystallinity calculated from melting enthalpies. Reference values of 205.0 and 146.6 J/g for completely crystallized PEO[35] and PHB[36] were used, respectively. [e] Temperature at which 10% of mass loss has occurred from TGA curves.

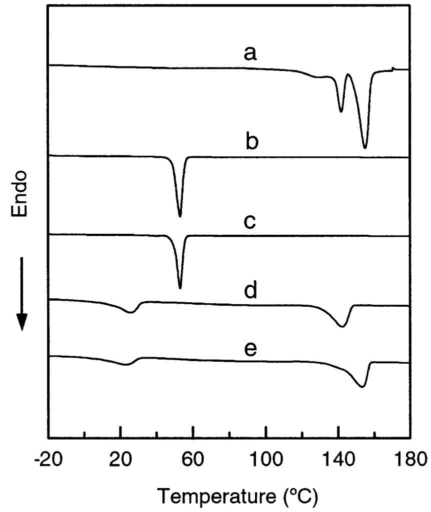


Figure 5. DSC second heating curves (5 °C/min) of (a) PHB-diol (M_n 3220), (b) M-PEO-A (M_n 1820), (c) EHE(20-05-20), (d) EHE(20-39-20), and (e) EHE(20-52-20).

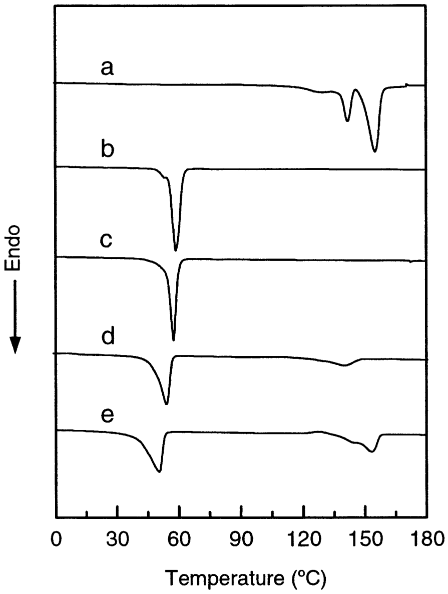


Figure 6. DSC second heating curves (5 °C/min) of (a) PHB-diol (M_n 3220), (b) M-PEO-A (M_n 4740), (c) EHE(50-08-50), (d) EHE(50-38-50), and (e) EHE(50-55-50).

of the PEO block decreases by ca. 27 °C from EHE-(20-05-20) to EHE(20-39-20) because the PEO block is relatively short and more subject to the effect of the PHB block, and there is also a steep change in PHB content from 11% to 52%. On the other hand, the melting temperature of the PEO block decreases modestly in the PEO−PHB−PEO triblock copolymer with PEO of molecular weight 5000, presumably because the PEO block is quite long as compared with the PHB block, and the change in PHB content in this series is also limited (Table 1).

Figures 7 and 8 show the XRD diagrams for the PEO and PHB precursors and the PEO−PHB−PEO triblock copolymers synthesized in this work. No reflection peaks for PHB block appear in the diagrams for copolymers with short PHB segments (Figures 7c and 8c), indicating that the PHB crystalline phase is not formed. For copolymers with longer PHB segments, the PHB block forms a separate crystalline phase similar to its PHB-diol precursor. The reflection peaks for PEO blocks indicate that the PEO crystalline phase in the copolymers presents a similar structure to its homopolymer. No PEO reflection peaks appear for EHE(20-38-20) and EHE(20-55-20) because their melting temperatures for PEO block are about room temperature (see Table 2), at which the XRD measurements were carried out. The XRD results agree well with those from the DSC measurements.

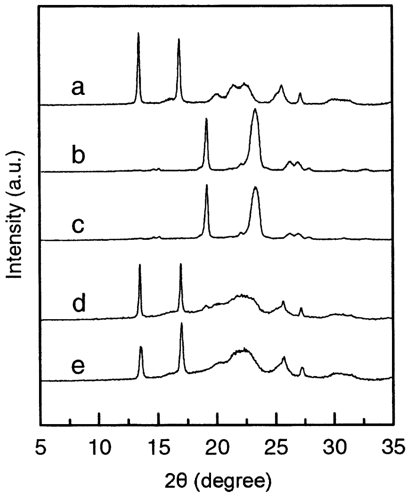


Figure 7. X-ray diffraction patterns for (a) PHB-diol (M_n 3220), (b) M-PEO-A (M_n 1820), (c) EHE(20-05-20), (d) EHE-(20-39-20), and (e) EHE(20-52-20).

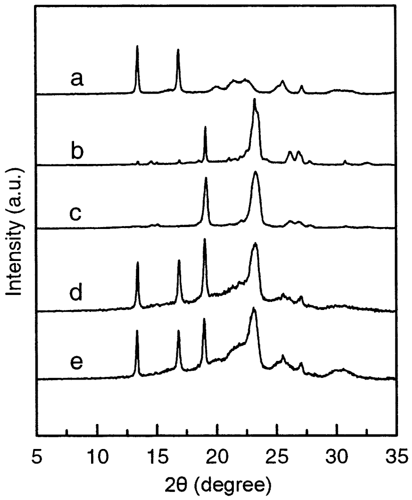


Figure 8. X-ray diffraction patterns for (a) PHB-diol (M_n 3220), (b) M-PEO-A (M_n 4740), (c) EHE(50-08-50), (d) EHE-(50-38-50), and (e) EHE(50-55-50).

Conclusions

New biodegradable amphiphilic PEO−PHB−PEO triblock copolymers have been successfully synthesized by coupling two chains of PEO with a low-molecular-weight isotactic PHB chain in the middle. The structures and molecular characteristics of the PEO−PHB−PEO triblock copolymers were studied by GPC, ^{1}H NMR, and FT-IR, which confirmed the ABA triblock chain architecture. Two series of triblock copolymers with PEO block lengths of M_n 1820 or 4740 were synthesized. Each series of triblock copolymers has middle PHB block lengths ranging from a few hundred to more than 5000, corresponding to PHB contents raging from 8 to 59% in weight. All of the triblock copolymers synthesized in this work have relatively narrow molecular weight distributions and unimodal peaks in the GPC chromatographs.

TGA analysis showed that the triblock copolymers undergo thermal degradation in two separate steps for the PHB and PEO blocks, from which the PHB contents were calculated, and the results were in good agreement with those determined from GPC and ^{1}H NMR. The TGA analysis also showed that the decomposition temperatures for each block in the copolymers are higher than their respective precursors, indicating that the triblock copolymers have better thermal stability.

Both DSC and XRD analyses showed that separate crystalline phases are formed by PEO and PHB blocks in the copolymers, except for EHE(20-05-20) and EHE-(50-08-50), in which the PHB block is too short. The crystallinity of PHB block in the copolymers increases as compared with the pure PHB precursor, presumably being caused by the presence of the soft PEO block. In contrast, the crystallinity of PEO block in the copolymers decreases as compared with the PEO precursor because of the presence of hard PHB block, which restricted the crystallization of the PEO blocks.

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