Synthesis and Characterization of Poly[(*R*,*S*)-3-hydroxybutyrate] Telechelics and Their Use In The Synthesis of Poly(methyl methacrylate)-*b*-Poly(3-hydroxybutyrate) Block Copolymers

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ABSTRACT: Poly[(*R*,*S*)-3-hydroxybutyrate] oligomers containing dihyroxyl (PHB-diol), dicarboxylic acid (PHB-diacid) and hydroxyl-carboxylic acid (a-PHB) end functionalities were obtained by the anionic polymerization of β-butyrolacton (β-BL). Ring opening anionic polymerization of β-BL was initiated by a complex of 18-Crown-6 with γ-hydroxybutyric acid sodium salts (for PHB-diol and a-PHB) or succinic acid disodium salt (for PHB-diacid). Dihydroxyl functionalization was formed by the termination of polymerization with bromo-ethanol or bromo-decanol while the others were done by protonation. Hydroxyl and/or carboxylic acid functionalized PHB oligomers with ceric salts were used to initiate the polymerization of methylmethacrylate (MMA). PHB-*b*-PMMA block copolymers obtained by this way were purified by fractional precipitation and characterized using ^{1}H-NMR and ^{13}C-NMR, gel permeation chromatography (GPC), and thermal analysis (DSC and TGA) techniques. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 965–973, 2002

Key words: β-Butyrolactone; PHB-diol; PHB-diacid; redox polymerization; PHB-*b*-PMMA

INTRODUCTION

PMMA is a very important and versatile polymeric material with many applications in surface coating industries and in the medical field. To insert biodegradable polymeric units via block/graft copolymerization technique into acrylate backbone enables polyacrylate modification for many biomedical applications and for environment protection. In our recent articles the grafting reactions of PMMA on poly(3-hydroxy nonanoate) (PHN) were reported. PHN is a member of medium chain length of the bacterial polyesters.[1,2] Elastomeric and biodegradable gain of PMMA via this modification were studied in detail. PMMA was also grafted onto medium chain length of polyhydroxyalkanoate containing double bonds in side chains in one shot free radical polymerization.[3,4] Redox polymerization of MMA using Ce(IV) with the commercial biodegradable oligo-diols such as polycaprolactone (PCL), polytetrahydrofuran (PTHF), poly glycidil azide

Table I   Results and Conditions of Anionic Polymerization of β-BL[a]

| Run. No. | Alkylating agent | | $[M_o]/[I_o]$[b] | Yield [%] | M_n[c] | M_w/M_n[c] |
	Type	Amount (mL)				
PHB-diol (HO-PHB-OH)						
3-I	HO(CH$_2$)$_2$Br	0.058	12	99	2300	1.2
3-II	"	0.082	9	82	1200	1.2
3-III	"	0.044	9	80	2100	1.2
3-IV	"	0.340	23	99	2600	1.1
3-V	"	0.697	9	99	1300	1.2
4-I	HO(CH$_2$)$_{10}$Br	0.162	12	81	2600	1.2
4-II	"	0.230	9	81	1400	1.3
4-III	"	0.123	9	81	2000	1.2
4-IV	"	0.950	23	99	2700	1.1
4-V	"	1.960	9	99	1500	1.2
a-PHBs (HO-PHB-COOH)						
a-PHB-VI	H$^+$		58	99	5500	1.1
a-PHB-VII	H$^+$		145	98	13000	1.2
PHB-diacid (HOOC-PHB-COOH)						
S6	H$^+$		4.6	80	966	1.1
S7	"		4.6	99	958	1.3
S8	"		4.6	90	910	1.0
S9	"		10.5	91	923	1.3
S10	"		5.2	71	837	1.3
S11	"		23.3	99	1334	1.4

[a] Polymerization was initiated by γ-hydroxybutyric acid sodium salts or succinic acid disodium salts/18-Crown-6 complex in order to obtain PHB oligomers containing dihydroxyl and/or dicarboxylic acid end functionalities.

[b] $[M_o]$: Molar concentration of β-BL, $[I_o]$: Molar concentration of the complex initiator. $[M_o]/[I_o]$ = Monomer/Initiator.

[c] Estimated by GPC experiments.

(PGA) was studied extensively in our recent publications.[5,6] Block copolymers containing 8–10 wt. % of oligomer units were obtained in this way.

Poly-(R)-3-hydroxybutyrate (PHB) as a member of bacterial polyesters is produced by a great variety of microorganisms as intracellular carbon and energy storage material.[7,8] PHB plays an important role in life processes and has various applications as a biodegradable polymer. Therefore there are many attempts to synthesize its synthetic analogue. Jedlinski et al.[9–11] produced PHB analogues via anionic ring opening polymerization of β-lactones using several kind of anionic initiators, naturally giving a-PHB containing a hydroxyl and a carboxylic acid group in the ends. In this manner, we reported for the first time the synthesis of the novel poly[(R,S)-3-hydroxybutyrate] telechelics containing primary hydroxyl groups at both polymer chain ends, via the termination of the ring-opening polymerization with bromo-decanol or bromo-ethanol.[12]

This article refers to the synthesis of the novel poly[(R,S)-3-hydroxybutyrate] telechelics containing carboxyl groups at both polymer chain ends via ring opening polymerization of β-butyrolactones and the synthesis of PHB-b-PMMA block copolymers using redox polymerization of MMA initiated with Ce(IV) and oligo PHB containing hydroxyl end group(s) and/or carboxyl end group(s).

EXPERIMENTAL

Materials

β-Butyrolactone was stored over CaH$_2$ for two days and distilled over Na under reduced pressure in an atmosphere of dry argon. The fraction boiling at 38°C (5 mmHg) was collected. 18-Crown-6 was purified by heating for 4 h under vacuum. THF was used without purification. CHCl$_3$ was dried by storing at Al$_2$O$_3$ (Aluminum

(A)

PHB-diol

a-PHB

bromoethanol; x=2, **3**
bromodecanol; x=10, **4**

(B)

PHB-diacid

Scheme 1
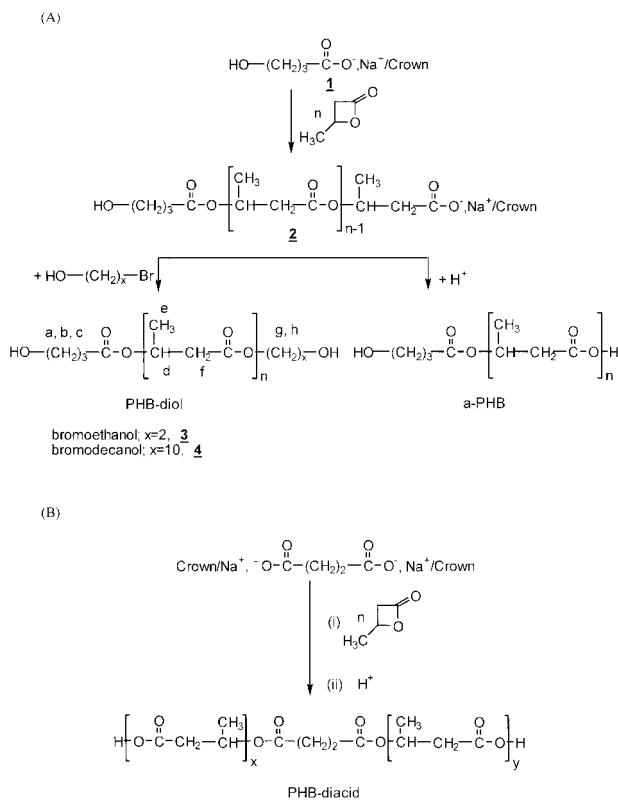
oxide 60 active) column under Ar gases for 2h. γ-Hydroxy butyric acid sodium salts and succinic acid disodium salts were used as received.

Methylmethacrylate (MMA) was supplied from Fluka A.G. and freed from inhibitor by vacuum distillation over CaH_2. Ceric ammonium nitrate, $Ce(NH_4)_2(NO_3)_6$, (CAN), was supplied from Fluka A.G. and used as received. 2-Bromoethanol ($d = 1.763$ g mL^{-1}), 10-bromodecan-1-ol (d = 1.19 g mL^{-1}) and tetrabutylammonium hydrogen sulfate (TBAHS) were supplied from Fluka A.G. and used as received.

All other chemicals were reagent grade and used as received.

Synthesis of PHB-diol and a-PHB Oligomers

PHB-diol and a-PHB oligomers were synthesized in Polish Academy of Sciences Research Laboratories using the following procedures reported in our recent article[12]:

Reactor was dried before use under vacuum by heating. The required amount of γ-hydroxy butyric acid sodium salt and THF were put into reactor and a few drops of water were added to dissolve the salt. To this solution was added 18-

Crown-6. After 1 h, the polymerization was initiated by introducing monomer (β-BL) to this solution at 17°C. The reaction was continued at room temperature for a week. The polymerization was monitored by GPC, ^{1}H-NMR, IR, and ESI-MS analysis. After the polymerization reactions were completed, the molecular weight of polymer was measured. Then 10% excess of equimolar amount of 2-bromoethanol (or 10-bromodecan-1-ol) was introduced with the polymer for termination to obtain PHB-diol oligomer **3** and **4**, respectively. The amounts of alkylating agent for each run were listed in Table I. For a-PHB oligomers (containing one hydroxyl end group), the last step of the reaction was terminated by the acid ion exchange resins (2–3 g) for two days without using any bromo-alifatic alcohols. After completion of the termination reactions, the polymers were precipitated in *n*-hexane.

Synthesis of Poly[(*R,S*)-3-hydroxybutyrate] Telechelics Containing Carboxyl Groups at Both Polymer Chain Ends
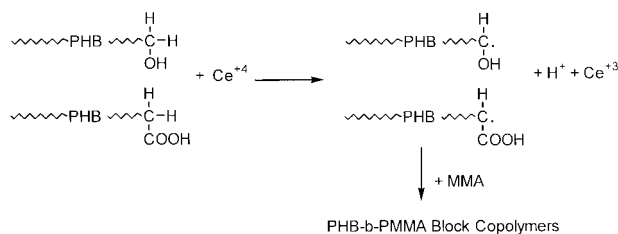
These oligomers were also synthesized in Polish Academy of Sciences Research Laboratories using the following procedures. The required amount of succinic acid disodium salt, THF and 18-Crown-6 were put into reactor. This mixture was stirred about 1 h, then a few drops of water were added to the reactor to dissolve the salt. After a few h, the polymerization of butyrolactone was initiated by introduction of monomer to this solution below room temperature. The polymerization was continued at room temperature and monitored by IR, GPC, ^{1}H-NMR, and ESI-MS analysis. Polymerization reactions were terminated with the acid ion exchange resin (Dowex 50 WX2).

Synthesis of Poly[(*R,S*)-3-hydroxybutyrate]-*b*-poly(methyl methacrylate) (PHB-*b*-PMMA) Block Copolymers

Polymerization was carried out in an inert nitrogen atmosphere at 40°C according to the procedure reported elsewhere.[5] The general experimental procedure was as follows: An appropriate amount of PHB was put in a pyrex tube, then a given amount of CAN solution and MMA were added to the tube. Approximately 10 mg of TBAHS was also added in order to increase the solubilities of MMA and PHB in the aqueous reaction media. Nitrogen was introduced for 1 min through a needle into the homogenous mixture to
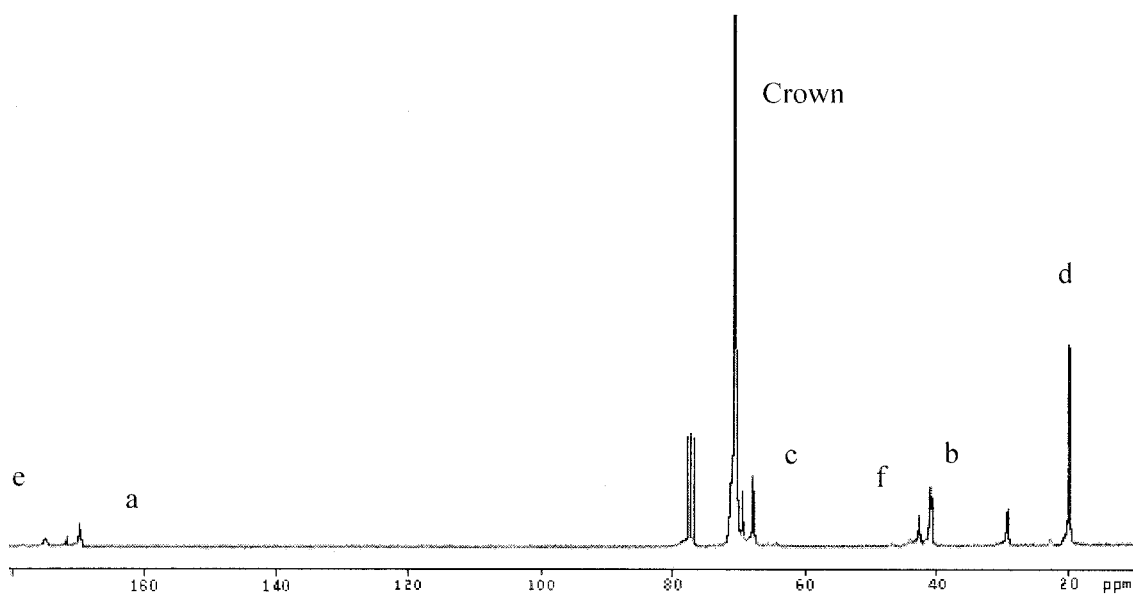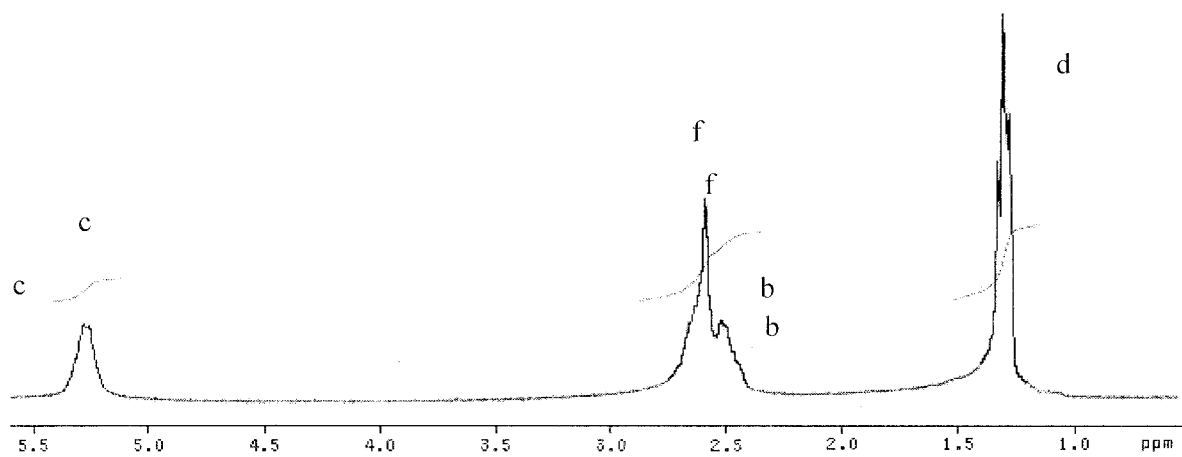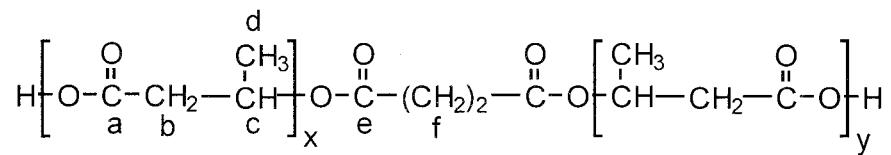
Figure 1   ¹H-NMR (top) and ¹³C-NMR (bottom) spectra of PHB-diacid oligomers (run number S7 in Table I).

Scheme 2

Figure 3 Effect of HNO_3 concentration on polymerization yield of MMA with PHB-diol. (■) run number 3-V (Mn = 1300), (●) run number 4-IV (Mn = 2700). [MMA] = 4.65 mol L^{-1}, [CAN] = 0.5 mol L^{-1}.

expel the air. The tube was covered with a stopper and kept at 40°C for a given time with stirring during the polymerization. After four h, the reaction mixture was precipitated in methanol, collected by filtration and dried to constant weight.

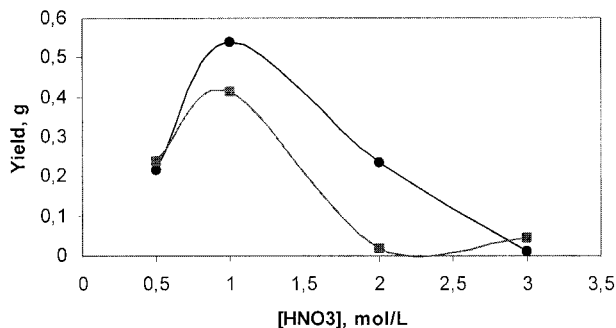### Purification of Block Copolymers by Fractional Precipitation Method

Pure block copolymers were isolated by fractional precipitation of chloroform solution of polymer with methanol from the crude polymer mixture. For this purpose, approximately 0.5 g of polymer was dissolved in 10 mL of $CHCl_3$. Methanol was gradually added to this solution until the polymer precipitated. γ-Values of block copolymers were calculated by taking volume ratio of nonsolvent (methanol) to solvent ($CHCl_3$).

Hydrolysis of PHB Units in the Block Copolymer Samples

An appropriate amount of block copolymer underwent by methanolysis by heating for 180 min under reflux condenser with 20 mL methanol containing 1 mL of 15% sulfuric acid and 1 mL of chloroform. An appropriate amount of block
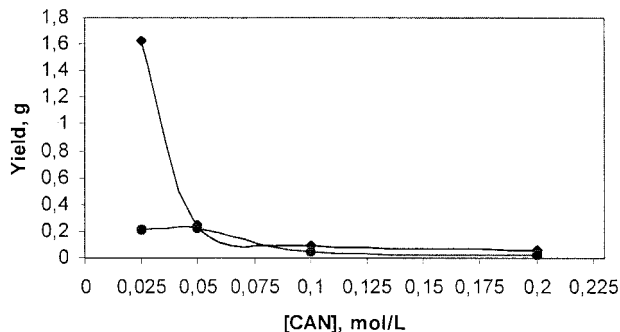
Figure 2 Effect of CAN concentration on polymerization yield of MMA with PHB-diol. (♦) run number 3-V (Mn = 1300), (●) run number 4 (Mn = 2700). [MMA] = 4.65 mol L^{-1}, [HNO_3] = 0.5 mol L^{-1}.

copolymer was also hydrolysed by heating for 180 min under reflux condenser with 20 mL of 15% KOH in methanol. PHB inclusion of block copolymers was calculated from the weight difference.

Instrumentation

NMR spectra were recorded using a Varian VCR-300 multinuclear spectrometer. The ^1H-NMR and ^{13}C-NMR spectra were run in $CDCl_3$ using TMS as an internal standard.

GPC experiments were conducted in THF solution at 35°C, at a flow rate of 1mL/min using a Spectra-Physics 8800 solvent delivery system with two MIXED-E styragel columns in series and a Shodex SE 61 refractive index detector. Polystyrene standards with low polydispersity were used to generate a calibration curve.

Differential scanning calorimetry, DSC, and thermogravimetric analysis, TGA, measurements were carried out under nitrogen atmosphere by using a Dupont DSC-9100 and Dupont TGA-951, respectively with a TA-9900 data processing system at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

PHB-diol, PHB-diacid, and a-PHB

PHB oligomers with hydroxyl and/or carboxylic acid end group(s) PHB-diol, a-PHB, and PHB-diacid were synthesized in high yields by the anionic ring opening polymerization of β-butyrolactones with γ-hydroxybutyric acid or succinic acid sodium salts/18-Crown-6 complex followed by termination with bromoethanol (or bromodecanol) or

Table II   Results and Conditions of the Polymerization of MMA by Ce^{IV}/PHB-diol Redox System at 40°C.

Run No.	Polymerization Initial Feed Concentration			Total Polymer Yield (g)	Block Copolymer Fractionation (wt %)
	PHB-diol ($M_n = 1323$; g)	[HNO_3] (mol/L)	Polym. time (h)		$\gamma_{2.8-5.5}$
116	0.102	3	4	No considerable polym. yield	—
155	0.1064	3	22	0.0444	—
115	0.104	0.5	4	0.010	—
117	0.101	0.5	22	0.240	74
119	0.203	0.5	22	0.667	57
120	0.504	0.5	22	2.255	70
122	2.004	0.5	22	2.838	58

[a] [MMA] = 4.65 mol L^{-1}.
[b] [Ce(IV)] = 0.05 mol L^{-1}.

H^+ as shown in Scheme 1. Table I lists the results and conditions of the anionic ring opening polymerization of β-butyrolactones initiated by γ-hydroxybutyric acid or succinic acid sodium salts/18-Crown-6 complex. Molecular weights of PHB oligomers were between 837 and 13000 Da. The tandem mass spectrometry analysis of the PHB-diols was also reported elsewhere.[12] ^{1}H-NMR spectra of PHB-diol and a-PHB, formulated in Scheme 1(A), showed the characteristic signals: δ(ppm): e: 1.3, b: 1.8–1.9, f+c: 2.4–2.7, a: 3.7, h: 3.8, g: 4.2, and d: 5.3, as reported before.[12] PHB oligomers with carboxyl end groups were synthesized by the anionic ring opening polymerization of β-butyrolactones with succinic acid disodium salts/18-Crown-6 complex followed by termination of polymerization by protonation (Scheme 1B). The polymerization proceeds at both ends of succinic acid disodium salts/18-Crown-6 complex. Table I also lists the results and conditions of the anionic ring opening polymerization of β-butyrolactones initiated by succinic acid disodium salts/18-Crown-6 complex. The telechelics with desired molecular weights were obtained depending on the monomer/initiator molar ratio. The ^{1}H-NMR and ^{13}C-NMR spectra of PHB-diacid reveal signals corresponding to poly(3-hydroxybutyrate) repeat units mentioned above and the sharp signal of succinic acid internal group at 2.5 ppm. Figure 1 shows the ^{1}H-NMR spectrum of the newly synthesized PHB telechelic: PHB-diacid.

PHB-*b*-PMMA Block Copolymers

The polymerization of methylmethacrylate (MMA) was carried out using a redox system consisting of Ce^{+4} ions and PHB oligomers.

Ce(IV) salts with several compounds including primary alcohols and carboxylic acids give radicals.[13–20] PHB-diol/Ce^{+4}, a-PHB/Ce^{+4} and PHB-diacid/Ce^{+4} redox couples were used in the copolymerization of MMA to obtain PHB–PMMA block copolymers, as shown in Scheme 2. Optimization studies of the redox polymerization were, first, done by changing CAN, HNO_3 concentrations, and the amount of PHB-diol oligomers. Effect of CAN concentration was studied by changing concentrations from 0.025 to 0.200 mol L^{-1}. Maximum copolymer yield was obtained at 0.025 mol L^{-1} for polymerization of MMA with 3V (Mn = 1300), and at 0.05 mol L^{-1} for polymerization of MMA with 4-IV (Mn = 2700) (Fig. 2). Effect of nitric acid concentration was also studied by changing concentrations from 0.5 to 3.0 mol L^{-1}. Maximum polymer yield was obtained at 1.0 mol L^{-1} HNO_3 concentration for this system (Fig. 3). Copolymer yield increased as the amount of PHB-diol oligomer was increased from 0.1 to 2.0 g (Run numbers 117, 119, 120, and 122 in Table II). Extension of the copolymerization time extensively influenced block copolymer yield. Polymer yield increases as polymerization time increases (compare run number 115 with 117, and number 116 with 155 in Table II). The polymer yield was also checked by using ceric ion alone in MMA polymerization at 40°C. As expected, we did not observe

Table III Results and Conditions of the Polymerization of MMA by Ce^{IV}/PHB Oligomers at 40°C.^{a}

| Run No.	Feeding of the Polymerization			Polym. Time (h)	Block Copolymer Fractionation, (wt. %)	
	a PHB ($M_n = 13000$; g)	a PHB ($M_n = 5500$; g)	PHB (COOH)$_2$ ($M_n = 837$; g)		Total Polymer Yield (g)	$\gamma_{2.3-5.0}$
128t	0.502	—	—	22	1.857	80
130	—	0.503	—	22	2.167	83
131	0.503	—	—	7	1.929	72
132	—	0.502	—	7	2.251	77
1	—	—	0.375	22	1.533	87
2	—	—	0.517	22	0.947	92
3	—	—	0.718	22	0.872	89

^{a} [MMA] = 4.65 mol L^{-1}, [Ce(IV)] = 0.05 mol L^{-1}, [HNO$_3$] = 0.5 mol L^{-1}.

any considerable polymer yield for 22 h polymerization time. TBAHS as surfactant indicated great effect in polymer yield; when copolymerization was conducted in the absence of TBAHS, no polymerization occurred for 22 h at 40°C. Block copolymers were purified by fractional precipitation. The volume ratio of the nonsolvent to solvent at the start of the polymer precipitation, γ value, of the block copolymer fractions ranged between 2.8 and 5.5, which is quite different from that of homo-PMMA (that is, γ = 3.0–3.9 for homo-PMMA), while PHB oligomers were soluble in a nonsolvent, methanol (γ > 14). The greater γ values of the block copolymers than that of homo-PMMA indicate the solubility effect of PHB oligomer in nonsolvent and confirms the block copolymer structure. The first fractions of the copolymers were all used in the characterizations. Homo-PMMA might not have occurred in this way because only radicals occur on the PHB-oligomers. The second fractions, which have higher γ values, are also block copolymers with lower molecular weights; the final very low fractions with γ > 14 were all unreacted PHB residues.

^{1}H-NMR and ^{13}C-NMR spectra of block copolymers reveal both characteristic signals of PHB and PMMA blocks. Figure 4 exhibits the ^{1}H-NMR spectrum of the copolymer sample of run number 128t in Table III. Characteristic peaks for PMMA and PHB blocks were observed (δ, ppm) at δ = 3.6 (due to —OCH$_3$ protons of MMA), δ = 1.9–2.0 (due to —CH$_2$— protons of MMA on the backbone), δ = 1.0–0.8 (due to —CH$_3$ protons of MMA), δ = 1.28–1.05 (due to —CH$_3$ protons of PHB), δ = 2.5–2.35 (due to —CH$_2$— protons of

PHB), δ = 5.25 (due to —CH—protons of PHB). Figure 5 exhibits the ^{13}C-NMR spectrum of the typical copolymer sample of run number 122 in Table II. Characteristic peaks for PMMA and PHB blocks were also observed in this case (δ, ppm) at δ = 16.5–18.7 (due to —CH$_3$ carbon in the main chain of PMMA), δ = 52.0 (due to CH$_3$ carbon in ester group of PMMA), δ = 44.6–44.9 (due to —CH$_2$— carbon of PMMA), δ = 177.7–178.0 (due to —C=O carbon of PMMA), δ = 19.7 (due to —CH$_3$ carbon of PHB), δ = 40.8 (due to —CH$_2$— carbon of PHB), δ = 67.6 (due to —CH— carbon of PHB), δ = 176.7 (due to —C=O carbon of PHB).

a-PHBs with one hydroxyl end group with Ce(IV) salt were also used in the vinyl polymer-
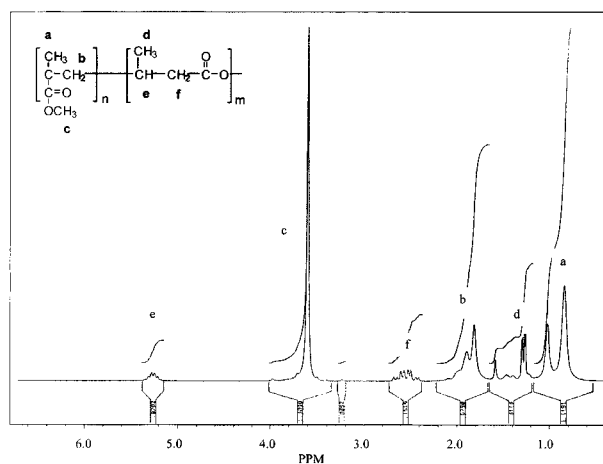
Figure 4 ^{1}H-NMR spectrum of PHB-*b*-PMMA copolymer (run number 128t in Table III.)
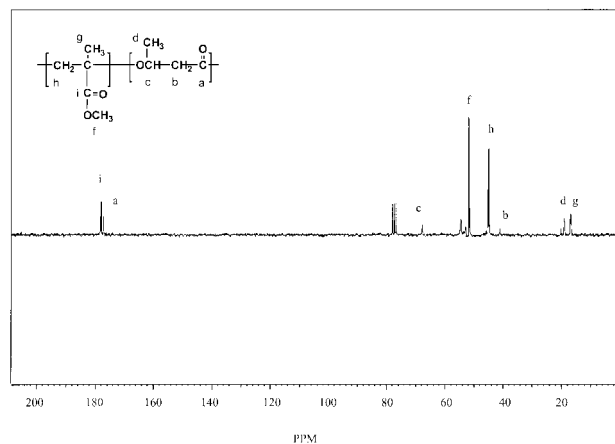
Figure 5 ^{13}C-NMR spectrum of PHB-*b*-PMMA copolymer (run number 122 in Table II.)

ization for 7 h and 22 h. Even short polymerization time (7 h) causes higher polymerization yields, which can be seen in Table III.

Molecular weights and PHB inclusions of block copolymers obtained using PHB-diol and a-PHB have been collected in Table IV. PHB content in block copolymers was calculated from ^{1}H NMR spectra and hydrolysis experiments. PHB-b-PMMA block copolymers varying 5–13 wt.−% of PHB contents were obtained by the redox polymerization. Methanolysis of ester groups of PHB in block copolymers can give a measure of PMMA blocks. So we can estimate whether the copolymer structure is AB or ABA type. Intrinsic viscosity of block copolymers before and after methanolysis were determined. The dramatic decrease of in-

trinsic viscosity of the hydrolyzed sample shows that the PHB blocks are in the middle of the copolymer chain, denoting an ABA type of block copolymer. For AB type of block copolymers, the intrinsic viscosity after hydrolysis changes slightly. The intrinsic viscosity of hydrolyzed sample is found to be 0.17 while the intrinsic viscosity of original sample is 0.40 (run number 119, Table II). The intrinsic viscosity of hydrolyzed samples of ABA type block copolymers change dramatically. As a result, PHB-diol leads to ABA type of block copolymer, while a-PHB leads to AB type of block copolymer, as expected.

Thermal analysis were carried out by DSC and TGA techniques. DSC results were also listed in Table IV. DSC curves of block copolymers exhibited three glass transitions $\approx$ 60°C, 12°C, and 114–120°C for block copolymers obtained using PHB-diol (run numbers 117, 119, and 120 in Table IV). However, block copolymers obtained using a-PHB also exhibited three T_g's around 28°C, 61°C, and 120°C (run numbers 128t, 130, 131, and 132 in Table IV). Higher T_g of PMMA blocks indicated that partly syndiotactic blocks were obtained by this method.[21] TGA curves exhibited two decomposition temperatures (T_d) for the block copolymer obtained by a-PHB at $\approx$ 250°C for PHB and at $\approx$ 330°C for PMMA segments and three decomposition temperatures for the block copolymer obtained by PHB telechelics at 210, 240, and 340°C. Figures 6a and 6b show the TGA curves of the block copolymer samples obtained using PHB-diol (run number 119) and a-PHB (run number 130 in Table III).

Table IV   Molecular Weights and Polymer Contents of the Block Copolymers

| | GPC | | | Block Copolymer Analysis (mol %) | | Thermal Analysis (DSC) | | | |
Run No.	$M_w \times 10^5$	$M_n \times 10^5$	M_w/M_n	PHB^a	PHB^b	T_{g1} (°C)	T_{g2} (°C)	T_{g3} (°C)	T_{g4} (°C)
117	3.0	1.5	2.03	—	—	−50	11	—	120
119	2.2	6.8	3.19	5	6	—	11	—	114
120	8.7	4.6	1.87	—	13	−65	12	—	115
122	7.4	1.9	3.84	—	6	—	28	57	117
128t	10.0	3.8	2.65	6	8	—	28	61	122
130	7.1	2.5	2.85	8	11	−53	29	63	110
131	8.4	1.7	4.91	6	8	—	29	61	—
132	4.9	1.2	4.14	—	8	—	29	62	118

^{a} Calculated from ^{1}H-NMR spectrum.
^{b} Calculated from methanolysis experiments.
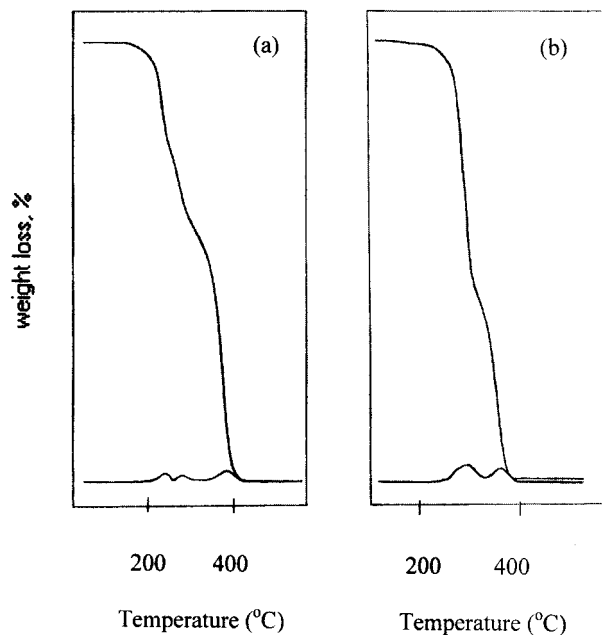
Figure 6 TGA curves of PHB-b-PMMA coplymers obtained using (a) PHB-diol (run number 119 in Table II), (b) using a-PHB (run number 130 in Table III).

CONCLUSIONS

PHB-diol, a-PHB and PHB-diacid can initiate the redox polymerization of MMA in the presence of Ce(IV) and yield PHB-b-PMMA in high yield. A surfactant such as TBAHS can increase solubility of the monomers in aqueous redox polymerization of hydrophobic monomers. PHB-b-PMMA block copolymers can be used as compatibilizers in PMMA and PHB polymer blends.

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