# Synthesis and Characterization of Diblock, Triblock, and Multiblock Copolymers Containing Poly(3-hydroxy butyrate) Units

**Hülya Arslan, Ayfer Menteş, Baki Hazer**

*Department of Chemistry, Zonguldak Karaelmas University, 67100 Zonguldak, Turkey*

**ABSTRACT:** A poly[(*R*,*S*)-3-hydroxybutyrate] macroinitiator (PHB-MI) was obtained through the condensation reaction of poly[(*R*,*S*)-3-hydroxybutyrate] (PHB) oligomers containing dihydroxyl end functionalities with 4,4′-azobis(4-cyanopentanoyl chloride). The PHB-MI obtained in this way had hydroxyl groups at two end of the polymer chain and an internal azo group. The synthesis of ABA-type PHB-*b*-PMMA block copolymers [where A is poly(methyl methacrylate) (PMMA) and B is PHB] via PHB-MI was accomplished in two steps. First, multiblock active copolymers with azo groups (PMMA-PHB-MI) were prepared through the redox free-radical polymerization of methyl methacrylate (MMA) with a PHB-MI/Ce(IV) redox system in aqueous nitric acid at 40°C. Second, PMMA-PHB-MI was used in the thermal polymerization of MMA at 60°C to obtain PHB-*b*-PMMA. When styrene (S) was used instead of MMA in the second step, ABCBA-type PMMA-*b*-PHB-*b*-PS multiblock copolymers [where C is polystyrene (PS)] were obtained. In addition, the direct thermal polymerization of the monomers (MMA or S) via PHB-MI provided AB-type diblocks copolymers with MMA and BCB-type triblock copolymers with S. The macroinitiators and block copolymers were characterized with ultraviolet–visible spectroscopy, nuclear magnetic resonance spectroscopy, gel permeation chromatography, cryoscopic measurements, and thermogravimetric analysis. The increases in the intrinsic viscosity and fractional precipitation confirmed that a block copolymer had been obtained. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1789–1796, 2004

**Key words:** azo polymers; block copolymers; polystyrene; radical polymerization

## INTRODUCTION

*Macroinitiator* is an abbreviation of *macromolecular initiator*, and it is based on the functional feature of a macromolecule. The selected functional groups of the macromolecule can be activated chemically, thermally, mechanochemically, photochemically, and so forth to yield active centers that initiate the polymerization of other monomers to produce block and graft copolymers.[1] Macroinitiators are precursors for the synthesis of block and graft copolymers (this depends on the site of initiation), and the advantage of this technique is that one component can be fully characterized before the preparation of block copolymers. Block copolymers can be prepared from various types of macroinitiators through radical and ionic polymerization. Macroinitiators generating radicals can be classified as macroazoinitiators (e.g., polyazocarbamates, polyazoamides, and polyazoesters), azoperoxidic initiators, redox macroinitiators,[2,3] macrophoto-initiators, and mechanochemical macroinitiators.[4] Several macroinitiators, such as macroazonitriles with polytetrahydrofuran units[5,6] and glycidylazide and epichlorohydrin moieties,[7] macroazoinitiators[8–10] with poly(ethylene glycol),[11–18] siloxane,[19,20] and poly(ε-caprolactone) units,[21,22] and azoperoxidic initiators with poly(ethylene glycol)[23,24] have been used successfully for the synthesis of block and graft copolymers via radical mechanism. Block copolymers with desired structures (AB- or ABA-type or multiphase block copolymers) and graft copolymers can be obtained with these macroinitiators.

Biopolyesters (PHAs) [poly(3-hydroxyalkanoates)] and other synthetic linear polyesters [e.g., polylactide, polycaprolactone, and poly(3-hydroxybutyrate)] are very interesting because of their biocompatibility, biodegradability, and permeability. However, these materials need chemical modification to improve their mechanical and viscoelastic properties for some medical and industrial applications. Chemical modifications have been achieved through the copolymerization, branching, and crosslinking of biodegradable polyesters.[25] The insertion of biodegradable units into industrially synthetic polymers [e.g., poly(methyl methacrylate) (PMMA) and polystyrene (PS)] is also important for chemical modification reactions of biodegradable polymers.

In this study, we attempted to insert poly[(R,S)-3-hydroxybutyrate] (PHB) units into commercially available polymers via the free-radical polymerization of methyl methacrylate (MMA) or styrene (S) initiated by macroazoinitiators containing PHB units.

## EXPERIMENTAL

### Materials

Poly[(R,S)-3-hydroxybutyrate] oligomers containing dihydroxyl end functionalities [PHB-diol; number-average molecular weight ($M_n$) = 1474] were synthesized through the anionic ring-opening polymerization of β-butyrolactone.[26] 4,4'-Azobis(4-cyanopentanoic acid) (ACPA) was supplied by Fluka, and phosphorus pentachloride (PCl$_5$) was supplied by Merck. Both were used without purification. MMA was supplied by Merck, and S was supplied by Aldrich. The monomers were freed from the inhibitor by vacuum distillation over CaH$_2$. Ceric ammonium nitrate [Ce(NH$_4$)$_2$(NO$_3$)$_6$ or CAN] was supplied by Fluka and was used after 1 h of drying at 105°C. Benzene was supplied by Carlo Erba and was purified by distillation and dried over Na before use. All other chemicals were reagent-grade and were used as received.

### Synthesis of the poly[(R,S)-3-hydroxybutyrate] macroinitiator (PHB-MI)

4,4'-Azobis(4-cyanopentanoyl chloride) (ACPC) was prepared through the reaction of ACPA with PCl$_5$. The pale yellow solid (mp = 96–99°C) was obtained and dried *in vacuo* at room temperature and was stored in a refrigerator.

A solution of 10 mmol (0.6551 g) of ACPC in 10 mL of dry benzene was gradually added to a mixture of 20 mmol (5.6106 g) of PHB-diol in 40 mL of dry benzene and 20 mmol (0.55 mL) of triethyl amine (NEt$_3$) with stirring at 0°C for 90 min in the dark. After an additional 3 h of stirring at 0°C in the dark, the reaction mixture was allowed to warm to room temperature, and then it was stirred overnight in the dark. The solvent was partially evaporated, and the obtained mixture was poured into petroleum ether. The macroinitiator was dissolved in CHCl$_3$ and then precipitated with petroleum ether; this procedure was repeated several times, and the pure macroinitiator was obtained. A reddish-brown, viscous liquid was obtained, and the product was dried *in vacuo* at room temperature. The yield was 5.7 g. The molecular weight of the product was determined by cryoscopic measurements from their benzene solutions.

### Synthesis of multiblock active copolymers with azo groups (PMMA-PHB-MI) via the redox polymerization of MMA with PHB-MI

Appropriate amounts of PHB-MI, a CAN solution (redox initiator), and MMA (monomer) were placed in a Pyrex tube. Approximately 10 mg of tetrabutyl ammonium hydrogen sulfate was also added to the mixture to increase the solubility of the monomer and diol in the aqueous reaction mixture. Argon was added for 1 min through a needle to the reaction mixture to expel the air, and the reaction tube was immersed in a water bath at 40°C for a given time with continuous stirring. After a fixed time of polymerization, the contents of the Pyrex tube were poured into methanol. The precipitated product was collected by decantation and filtration and dried *in vacuo* at 30°C. Thus, PMMA-PHB-MI was obtained, and then it was separated from related homopolymers by fractional precipitation.

### Thermal polymerization of the vinyl monomers

Appropriate amounts of a pure macroazoinitiator (PMMA-PHB-MI or PHB-MI) and monomer (MMA or S) were placed in a Pyrex tube. Argon was added for 1 min through a needle to the reaction mixture to expel the air, and the reaction tube was immersed in a water bath at 60°C for a given time with continuous stirring. The product was precipitated in methanol, collected by decantation and filtration, and dried *in vacuo* at 30°C. Block copolymers were obtained, and then they were separated from the related homopolymers by fractional precipitation.

### Instrumentation

^{1}H-NMR spectra were recorded with a Varian VCR-300 multinuclear spectrometer in CDCl$_3$ with tetramethylsilane as an internal standard.

Gel permeation chromatography (GPC) experiments were conducted in a tetrahydrofuran solution at 35°C at a flow rate of 1 mL/min with a Spectra Physics 8800 solvent-delivery system with two mixed-E Styragel columns in series and a Shodex SE 61 refractive-index detector. PS standards of low polydispersity were used to generate a calibration curve.

Fourier transform infrared (FTIR) spectra were recorded with a Jasco FT/IR-300 E FTIR spectrophotometer with chloroform as a solvent.

Ultraviolet–visible (UV–vis) spectra were recorded with a Unicam mark spectrophotometer and an Epson Mark FX-870 recorder.

A Cannon 1C A718 Ubbelohde viscometer was used for the viscosity measurements of the polymers. The measurements were performed at 30°C with chloroform as a solvent. Thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere with a
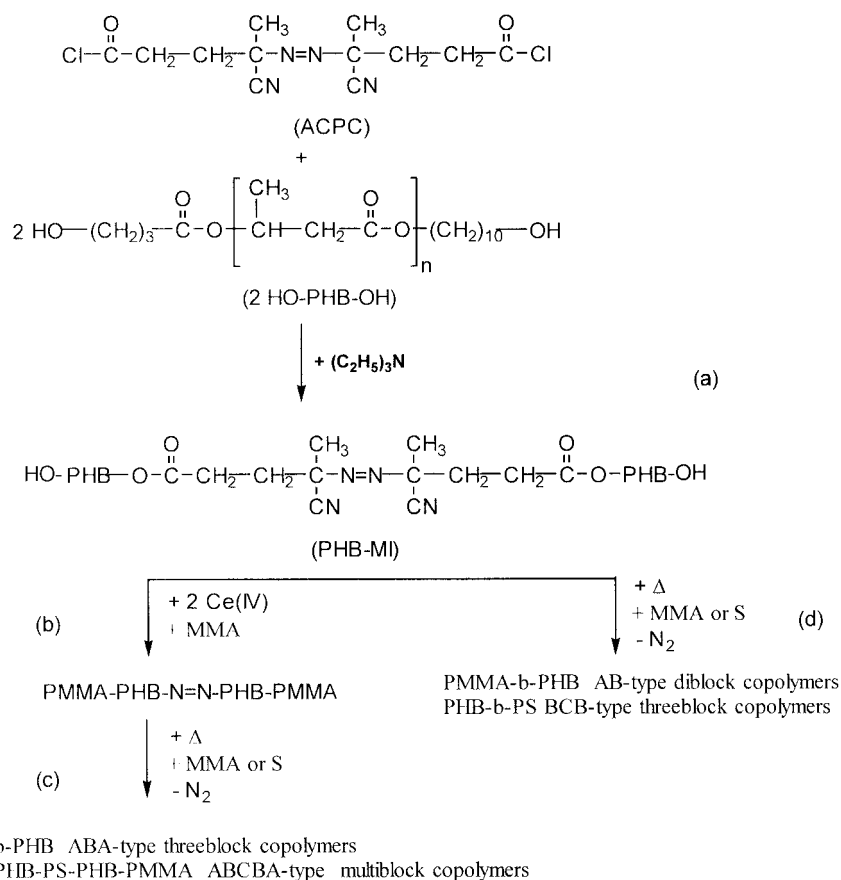
**Scheme 1**

DuPont TGA 951 with a TA 9900 data processing system at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Synthesis of the macroazoinitiators

PHB-MI was obtained through the condensation reaction of PHB-diol with ACPC [Scheme 1(a)]. During the preparation of polyazoesters from PHB and ACPC in a 2:1 molar ratio, 30% chain extension occurred, which was acceptable.[27] Then, the free-radical polymerization of MMA was initiated by a ceric ion/PHB-MI redox pair to obtain PMMA-PHB-MI [i.e., macroazoinitiators containing PHB and PMMA units; Scheme 1(b)]. The molecular weights of PHB-MI were determined by cryoscopic measurements from benzene solutions and were approximately twice that of PHB-diol (Table I). This demonstrated the formation of macroazoinitiators according to Scheme 1(a). The results and conditions of the redox free-radical polymerization of MMA are collected in Table II. The yields were quite high in these systems. PMMA-PHB-MI was isolated from related homopolymers by fractional precipitation with chloroform as a solvent and methanol as a nonsolvent. The γ values of the

polymers were also determined as the ratio of the volume of the chloroform solution to the volume of methanol: $\gamma = \infty$ for PHB-diol (because of the solubility of these oligomers in methanol) and $\gamma = 3.0–3.9$ for homo-PMMA. Of the polymers, 66–81 wt % was precipitated between $\gamma = 2.9$ and $\gamma = 4.3$. There was a slight difference from the γ value of homo-PMMA coming from the PHB concentration. The PHB-MI res-

**TABLE I**
**Synthesis of PHB-MI by the Condensation Reaction of PHB-Diol with ACPC**

| Run | Initial feed concentration | | | Yield (g) | Macroinitiators | |
| | PHB-diol | | ACPC (g) | | $M_n$[a] | $M_n$[b] |
| | $M_n$ | g | | | | |
|---|---|---|---|---|---|---|
| PHB-MI-1 | 1474 | 5.89 | 0.63 | 2.73[c] | 3192 | 2250 |
| PHB-MI-2 | 1474 | 5.61 | 0.65 | 5.70 | 3192 | 2400 |

[a] Calculated theoretically.
[b] Determined by cryoscopic measurements from benzene solutions.
[c] The purification procedure, containing several steps, such as washing with a 15 wt % HCl aqueous solution and drying over Na₂SO₄, was different from that for PHB-MI-2, so there was a loss of polymer in that case.

**TABLE II**
**Synthesis of PMMA-PHB-MI via Free-Radical Polymerization of MMA Initiated by**
**the Ce(IV)/PHB-MI Redox System at 40°C for 4 h**

| Run | PHB-MI | | Yield (g) | PHB-PMMA-MI fractionation (wt %) | | |
|-----|--------|---|-----------|----------------------------------|---|---|
|     | Type | g | | $\gamma 2.9–4.3$ | $M_n \times 10^3$ [a] | $M_w \times 10^3$ |
| 1-3 | PHB-MI-1 | 0.614 | 1.72 | 81 | 128.3 | 472.6 |
| 2-1 | PHB-MI-2 | 0.604 | 1.53 | 68 | 139.6 | 408.9 |
| 2-2 | PHB-MI-2 | 1.057 | 2.62 | 66 | 195.5 | 627.2 |

[HNO$_3$] = 0.5$M$; [CAN] = 0.05$M$; [MMA] = 4.65$M$.
[a] The molecular weights of PHB-PMMA-MI were determined by GPC.

idue, which was a small fraction at $\gamma > 14$, was also determined from the physical properties of the product.

**Thermal copolymerization**

In this case, the azo groups in the macroinitiators were cleaved thermally at 60°C. Therefore, ABA-type PMMA-*b*-PHB triblock copolymers for the thermal polymerization of MMA and ABCBA-type multiblock copolymers with PS units in the middle for the thermal polymerization of S were obtained with PMMA-PHB-MI [Scheme 1(c)]. For the thermal polymerization of the monomers (MMA or S) with PHB-MI, AB-type PHB-*b*-PMMA diblock copolymers and BCB-type PHB-*b*-PS triblock copolymers were obtained [Scheme 1(d)]. The thermal polymerization conditions and results are given in Table III.

The pure block copolymers were isolated from related homopolymers by fractional precipitation. During the fractional precipitation of AB- and ABA-type PMMA-*b*-PHB block copolymers, 70–97 wt % of the pure block copolymers was precipitated between $\gamma$ = 2.8 and $\gamma$ = 4.4. The $\gamma$ values of the block copolymers included the $\gamma$ values of homo-PMMA and changed according to the weight percentages of PHB

and PMMA in the copolymer structure. Of the PHB-*b*-PS pure block copolymer (BCB-type), 72 wt % was precipitated between $\gamma$ = 0.4 and $\gamma$ = 0.8, whereas $\gamma$ was 0.4–0.9 for homo-PS. This could be explained by the higher PS concentration in the copolymer. However, for ABCBA-type PMMA-*b*-PHB-*b*-PS multiblock copolymers, 70 wt % was precipitated between $\gamma$ = 2.5 and $\gamma$ = 3.0, that is, between the precipitation intervals of homo-PS and homo-PMMA.

The molecular weights of the block copolymers were determined by GPC analysis and are listed in Table III. Viscosity measurements were also performed on the copolymers. The block copolymers had higher intrinsic viscosities than the multiblock active copolymers (cf. runs 2-1 and 2-1-2, 2-2 and 2-2-2, and 1-3 and 1-3-1, Table III) because of their higher molecular weight. When the molecular weights and intrinsic viscosities of runs 2-1 (PHB-MI), 2-1-1 (PHB-*b*-PMMA), and 2-1-2 (PHB-*b*-PMMA) were compared, we found that the intrinsic viscosities of the polymers changed linearly with the molecular weights of the polymers. Additionally, an increase in the molecular weights and intrinsic viscosities of the polymers confirmed the formation of a block copolymer structure.

All characterizations were performed on first fractions, which were pure block copolymer fractions.

**TABLE III**
**Thermal Polymerization of MMA and S by Macroazoinitiators Containing PHB Groups at 60°C**

| | Polymerization initial feed concentration | | | | | | | | | | GPC anlaysis of block copolymers | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Macroinitiators | | | | | | | | | | | | |
| | PHB-MI | | PHB-PMMA-MI | | | MMA | S | Time | Yield | | | | |
| Run | Type | g | Type | g | [$\eta$] | (mL) | (mL) | (h) | (g) | [$\eta$] | $M_w \times 10^3$ | $M_n \times 10^3$ | Poly dispersity |
| 1-1 | 1 | 0.73 | — | — | — | 3 | — | 3 | 2.56 | — | 858.2 | 247.7 | 3.5 |
| 1-2 | 1 | 0.74 | — | — | — | — | 3 | 3 | 0.50 | — | 70.6 | 31.2 | 2.3 |
| 1-3-1 | — | — | 1–3 | 0.32 | 1.20 | 2 | — | 5 | 0.28 | 1.55 | 644.3 | 431.3 | 1.5 |
| 1-3-2 | — | — | 1–3 | 0.52 | 1.20 | 2 | — | 5 | 0.47 | 1.26 | 657.2 | 428.7 | 1.5 |
| 1-3-3 | — | — | 1–3 | 0.15 | 1.20 | — | 2 | 5 | 0.13 | — | 975.0 | 286.3 | 2.1 |
| 2-1-1 | — | — | 2–1 | 0.25 | 0.85 | 2 | — | 5 | 0.24 | 1.12 | 582.4 | 279.9 | 2.1 |
| 2-1-2 | — | — | 2–1 | 0.51 | 0.85 | 2 | — | 5 | 1.45 | 2.56 | 2634.8 | 514.5 | 5.1 |
| 2-2-1 | — | — | 2–2 | 0.26 | 1.23 | 3 | — | 5 | 2.04 | 2.76 | — | — | — |
| 2-2-2 | — | — | 2–2 | 0.50 | 1.23 | 3 | — | 5 | 2.54 | 2.53 | 2504.3 | 590.8 | 4.2 |
| 2-2-3 | — | — | 2–2 | 0.25 | 1.23 | — | 2 | 5 | 0.26 | — | 1284.1 | 420.6 | 2.7 |
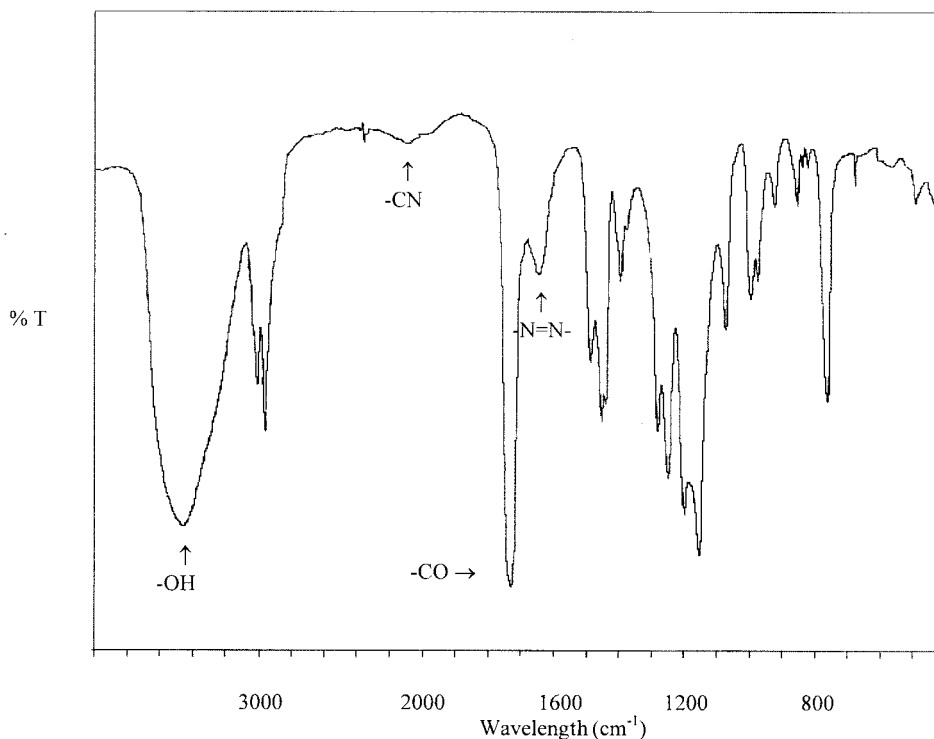
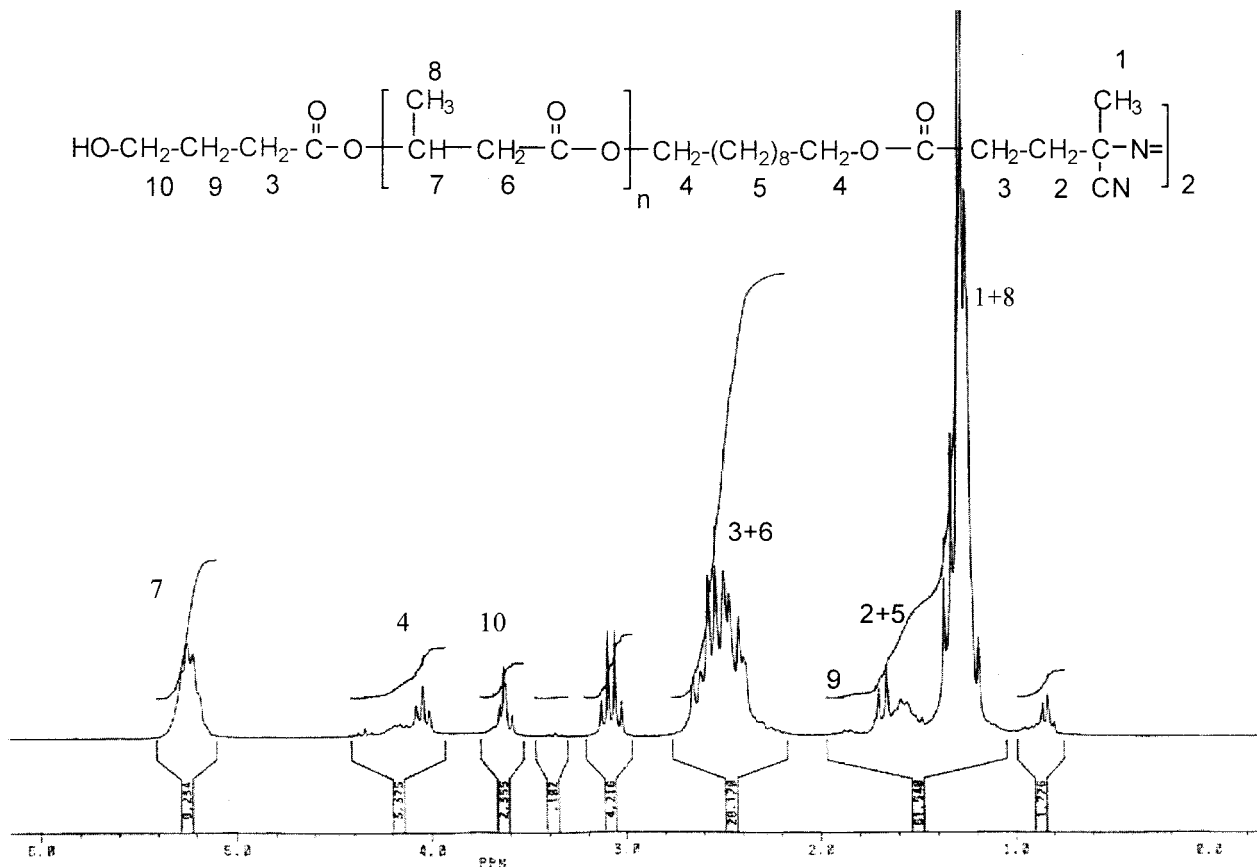**Figure 1**   FTIR spectrum of PMMA-PHB-MI (run 1-3, Table II).



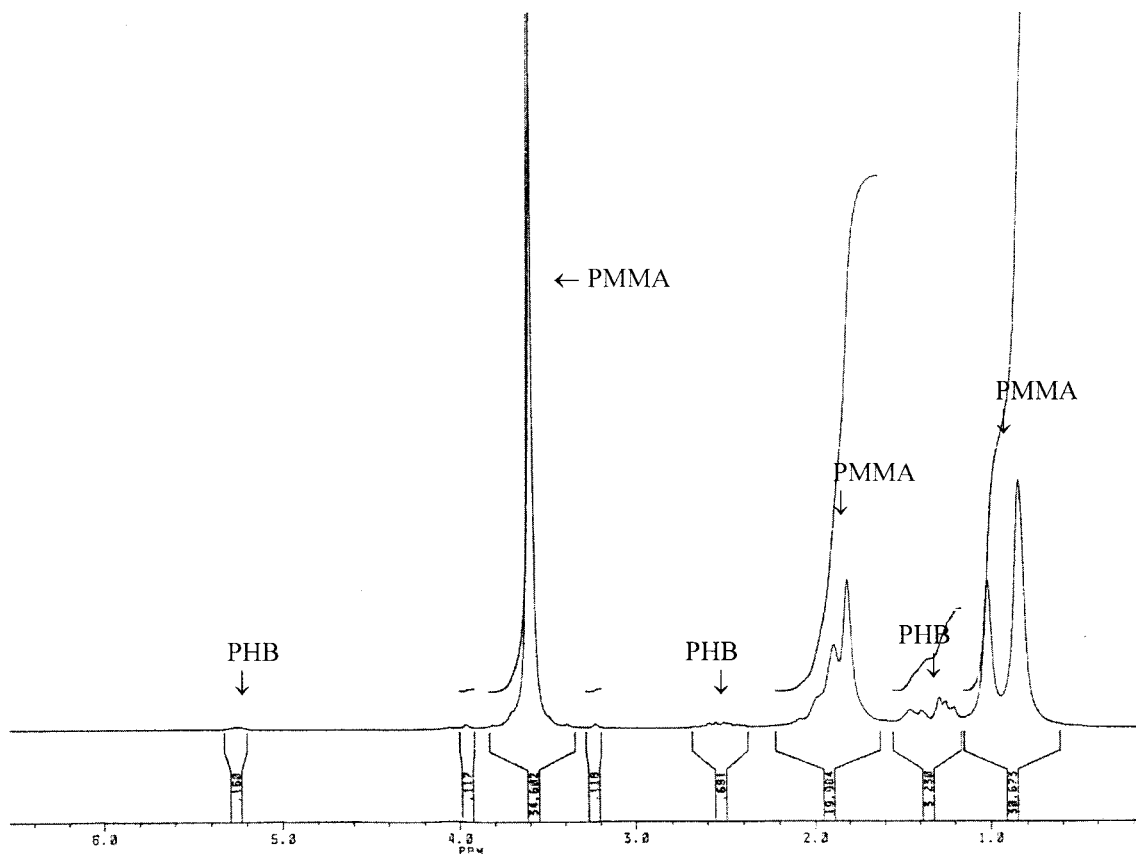**Figure 2**   $^1$H-NMR spectrum of PHB-MI (run 2, Table II).

**Figure 3** ¹H-NMR spectrum of PMMA-PHB-MI (run 2-2, Table II).

UV–vis analyses were also performed. Because PHB-MI and PMMA-PHB-MI had chromophore groups such as C=O and N=N, whereas PHB-*b*-PMMA block copolymers had only C=O groups, the UV–vis spectra of PHB-MI (run 2, Table III) had two absorption peaks (at 246 nm for C=O and at 266 nm for N=N groups), whereas PHB-MI (run 1, Table III) had only one strong, broad absorption band (at 252 nm). A strong, broad absorption band between 200 and 300 nm demonstrated the conjugation of two chromophore groups at least. UV–vis spectra of PMMA-PHB-MI (runs 1-3, 2-1, and 2-2, Table III) also exhibited two absorption peaks (at 240 and 273 nm for C=O and N=N groups, respectively). PHB-*b*-PMMA block copolymers, obtained thermally [Scheme 1(c)], exhibited only one adsorption peak for the C=O group. The UV–vis results demonstrated that the reaction mechanism in Scheme 1 proceeded successfully.

The spectroscopic characterization of the macroazoinitiators (PHB-MI and PMMA-PHB-MI) and copolymers was performed with FTIR and NMR analysis. The spectroscopic analysis of the products also confirmed that the related reaction mechanism proceeded successfully and that both polymer segments were present in the block copolymer structure. In the

FTIR spectra of PHB-MI and PMMA-PHB-MI, the adsorption peaks of —N=N— and —CN groups pertaining to the macroazoinitiator were observed at 1630 and 2100 cm⁻¹, respectively. In this spectrum, a strong absorption peak observed at 1730 cm⁻¹ and a broad absorption peak at 3400–3600 cm⁻¹ were due to C=O and OH groups, respectively (Fig. 1). The ¹H-NMR spectrum of PHB-MI (run 2, Table II) exhibited the characteristic peaks of this structure (Fig. 2). The ¹H-NMR spectrum of PMMA-PHB-MI (run 2-2, Table II) also revealed the characteristic peaks of PHB and PMMA block segments of the copolymer (Fig. 3). In the ¹H-NMR spectrum of PMMA-PHB-MI, characteristic peaks for PMMA [δ = 3.6 (—OCH₃ protons) 1.9–2.0 (—CH₂— protons), and 0.8–1.0 ppm (—CH₃ protons)] and characteristic peaks for PHB [δ = 1.28 (—CH₃ protons), 2.5 (—CH₂— protons), and 5.25 ppm (—CH— protons)] were observed. The ¹H-NMR spectrum of the PMMA-PHB-PS-PHB-PMMA multiblock copolymers (run 2-2-3, Table III) revealed the characteristic peaks of PS blocks at approximately 6.6 and 7.1 ppm, in addition to the ¹H-NMR spectrum of PMMA-PHB-MI (run 2-2, Table II). Because of the reduction in the PHB proportion in the copolymer structure with the insertion of PS into the PMMA-PHB-MI structure via copolymerization, the intensity of the peaks corre-
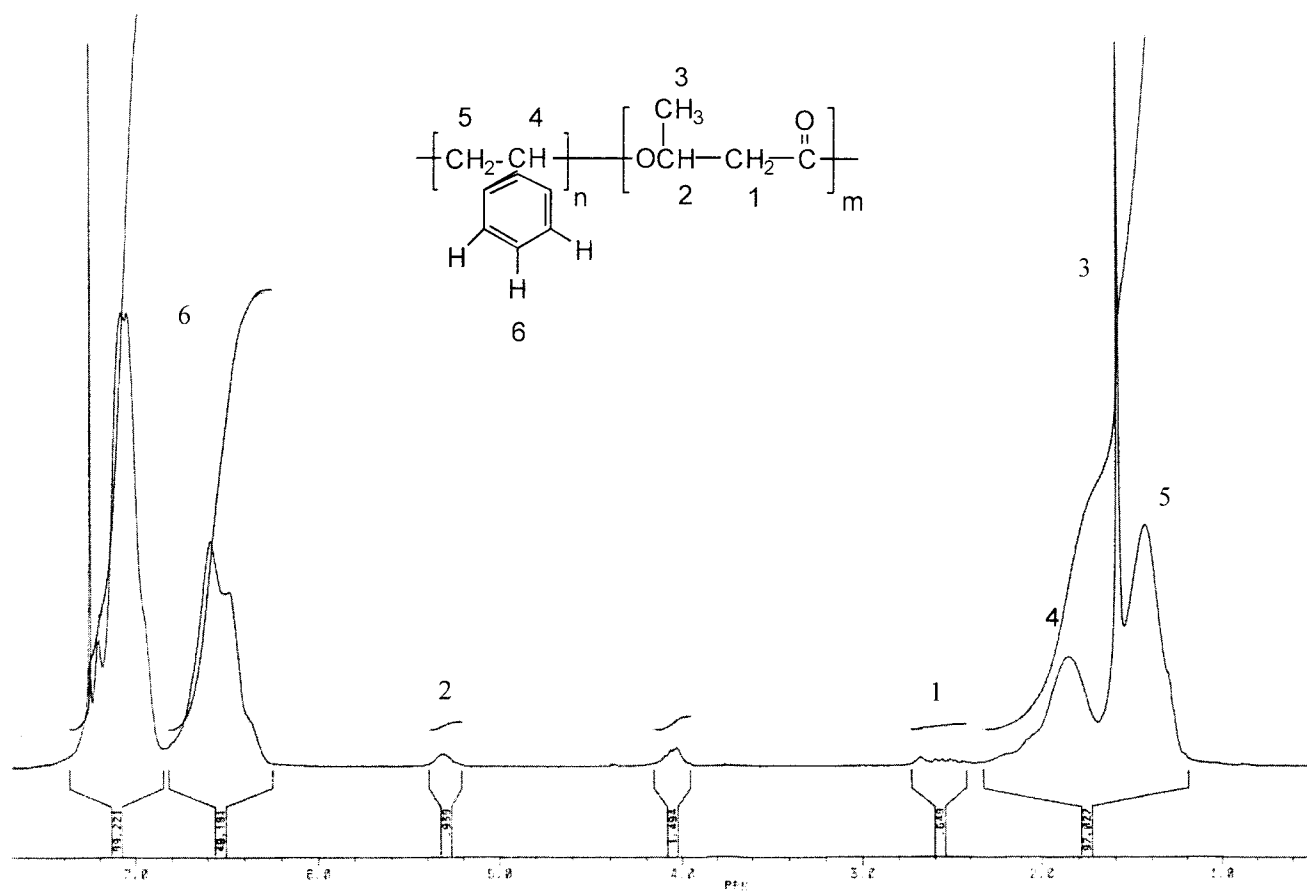
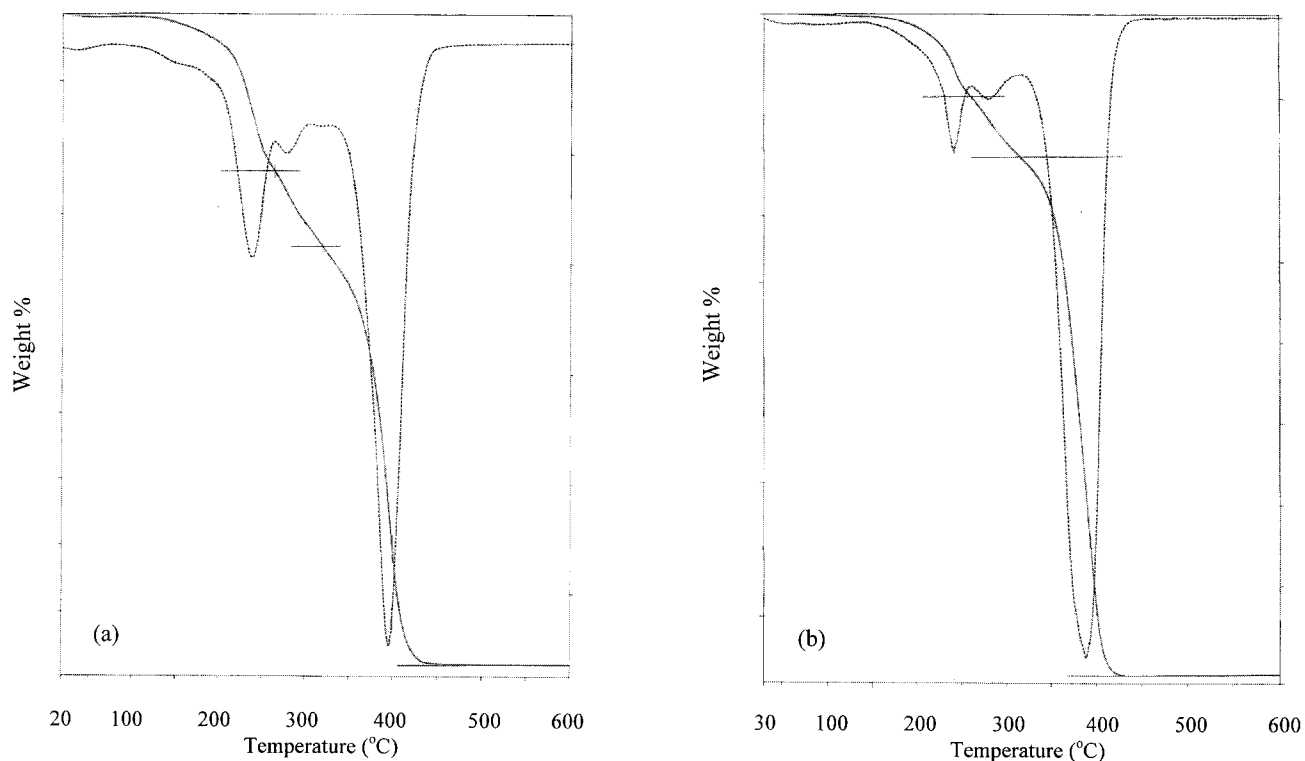**Figure 4**   $^1$H-NMR spectrum of PS-*b*-PHB (run 1-2, Table III).

**Figure 5**   TGA thermograms of (a) PMMA-PHB-MI (run 2-1, Table II) and (b) PHB-*b*-PMMA (run 2-1-2, Table III).

sponding to PHB decreased, and even the peaks could not be observed. The ^{1}H-NMR spectrum of PS-*b*-PHB also exhibited characteristic peaks of PHB and PS blocks of the copolymers (Fig. 4).

The thermal characterization of the polymers was performed by TGA. TGA thermograms of PMMA-PHB-MI exhibited four decomposition temperatures ($T_d$'s), around 240, 280, 315, and 390°C, for PHB and PMMA segments and a small peak around 105–140°C for the evaporation of residual solvent and nonsolvent used in the purification of the macroinitiators or the decomposition of the diazo groups of the macroinitiators.[7] TGA thermograms of the triblock copolymers (ABA) exhibited three $T_d$'s around 240, 280, and 380°C (Fig. 5). TGA thermograms of ABCBA-type multiblock copolymers were similar to TGA thermograms of ABA-type triblock copolymers, and so $T_d$'s of PMMA and PS were close. The PHB concentrations of the products were calculated from TGA thermograms and were around 5–9 mol %. The PHB concentrations of the products were not calculated via ^{1}H-NMR because the peaks of PHB were very small.

## CONCLUSIONS

AB- and ABA-type PMMA-*b*-PHB block copolymers and ABCBA-type PMMA-*b*-PS-*b*-PHB block copolymers were prepared with PHB macroazoinitiators. Biodegradable polymeric units such as PHB could be inserted into the PMMA (and PS) block in this way to obtain biobased polymeric materials that were environmentally friendly.

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