The Synthesis of Poly(3-hydroxybutyrate)-*g*-poly(methylmethacrylate) Brush Type Graft Copolymers by Atom Transfer Radical Polymerization Method

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ABSTRACT: Brush type of poly (3-hydroxy butyrate), PHB, copolymer synthesis has been reported. Natural PHB was chlorinated by passing chlorine gas through PHB solution in $CHCl_3/CCl_4$ mixture (75/25 v/v) to prepare chlorinated PHB, PHB-Cl, with the chlorine contents varying between 2.18 and 39.8 wt %. Toluene solution of PHB-Cl was used in the atom transfer radical polymerization (ATRP) of methyl methacrylate, MMA, in the presence of cuprous bromide (CuBr)/2,2′-bipyridine complex as catalyst, at 90°C. This ''grafting from'' technique led to obtain poly (3-hydroxybutyrate)-g-poly(methylmethacrylate) (PHB-*g*-PMMA) brush type graft copolymers (cylindrical brush). The polymer brushes were fractionated by fractional precipitation methods and the γ values calculated from the ratio of the volume of nonsolvent to volume of solvent of brushes were ranged between 2.8 and 9.5 depending on the molecular weight, grafting density, and side chain length of the brushes, while the γ values of PHB, PHB-Cl, and homo-PMMA were 2.7–3.8, 0.3–2.4, and 3.0–3.9, respectively. The fractionated brushes were characterized by gel permeation chromatography, ^{1}H-NMR spectrometry, thermogravimetric analysis (TGA), and differential scanning calorimetry techniques. PHB-*g*-PMMA brush type graft copolymers showed narrower molecular weight distribution (mostly in range between 1.3 and 2.2) than the PHB-Cl macroinitiator (1.6–3.5). PHB contents in the brushes were calculated from their TGA thermograms and found to be in range between 22 and 42 mol %. The morphologies of PHB-*g*-PMMA brushes were also studied by scanning electron microscopy. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1742–1750, 2007

Key words: polymer brush; poly(3-hydroxybutyrate)-*g*-poly(methylmethacrylate); (PHB-*g*-PMMA); PHB-Cl macro initiator; ATRP

INTRODUCTION

Poly (3-hydroxy alkanoate)s, PHAs, are naturally biodegradable polyesters produced as intracellular energy and carbon storage materials by a wide variety of microorganisms and have the following general structure[1–3]:
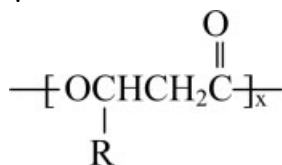
In which R is an alkyl side chain of naturally occuring PHAs depending on the substrates and the type of the bacteria. There are two types of PHAs according to the length of the *R* alkyl chain, that is, either a short chain length, *scl*PHA with an alkyl side chain having 1–2 carbon, produced by *Ralstonia eutropha* or a medium chain length, *mcl*PHA with an alkyl side chain having higher than 3 carbon atom, produced by *Pseudomonas oleovorans*. Various types of PHAs with diverse physical properties have been produced using alkanols, alkanoic acids, edible oily acids, bromo and phenyl derivatives of alkanoic acids.[4–11]

The bacterial poly (3-hydroxy butyrate) (PHB) (R=CH₃) generally has molecular weight from 10^5 to 10^6 and is a thermoplastic with the melting temperature at 177°C. However, it is a highly crystalline and brittle polymer with low elongation before breaking, of which properties result in the limited application. In contrast, Poly(3-hydroxy octanoate) (PHO), as a member of the *mcl*PHAs, is a thermoplastic with the melting temperature at 61°C. It is soft and elastomeric polymer. PHAs have many medical and industrial applications because of their biocompatibility, biodegradability, and permeability.[12] To improve the physical and mechanical properties, PHAs need modification. Grafting on the PHAs and functionalization of PHAs can be performed via chemical reactions.[13–23]

Graft copolymers exhibit good phase separation and are used for a variety of applications, such as impact-resistant plastics, thermoplastic elastomers,

compatibilizers, and polymeric emulsifiers. Because of their branched structure they generally have lower melt viscosities, which is advantageous for processing. They have great potential to realize new properties because of their structural variables (composition, backbone length, branch length, branch spacing, etc.).[24] When relatively high grafting density is obtained they are called as polymer brushes.

Polymer brushes are typically synthesized by two different methods: physisorption and covalent attachment. Covalent attachment is preferred as it overcomes the disadvantages of physisorption, which include thermal and solvolytic instabilities. Covalent attachment of polymer brushes can be achieved by either ''grafting to'' or ''grafting from'' techniques. In the ''grafting to'' method preformed polymer chains containing a suitable end-functionalized group are reacted with a surface to obtain the desired brush. The ''grafting from'' technique involves the immobilizing of initiators onto the substrate followed by in situ surface-initiated polymerization to generate the tethered polymer brush. The ''grafting from'' approach has generally become the most attractive way to prepare thick, covalently tethered polymer brushes with a high grafting density. There are several major parameters that control the brush properties: the degrees of polymerization of the main (DPn) and side chains (DPsc), grafting density, chain length, and chemical composition of the chains. Recently, the synthesis of polymer brushes has great attention due to their unique properties and applications, such as the fabrication of molecular electronic and optical devices and the prevention of ion etching, colloid stabilization, chemical gates, drug delivery, biomimetic materials, modification of lubrication, friction, adhesion, and wet ability of surfaces.[25–29] A variety of synthetic methods such as reverse atom transfer radical polymerization,[30] living anionic surface initiated polymerization,[31] atom transfer radical polymerization (ATRP),[26,27,32–36] dispersion polymerization,[37] aqueous atom transfer radical polymerization,[38] reversible addition fragmentation transfer (RAFT) polymerization for the preparation of polymer brushes have been proposed.

ATRP is one of the well-developed controlled living polymerization and it has been attracting much attention as a new route to well-defined polymers with low polydispersities. Many studies have been reported in the literature about the synthesis of macromolecules with various compositions (homopolymers, random, periodic, block, graft, and gradient copolymers) and novel topologies (linear, star, comb, branched, hyper branched, networks, brushes etc.) using ATRP.[39–59]

In our laboratory *mcl* and *scl*PHAs including PHB have been chlorinated to obtain new modified chlorinated polyesters[60,61] and chemical modification of

chlorinated microbial polyesters was extended by converting of PHA-Cl to their corresponding quaternary ammonium salts, sodium sulphate salts, and phenyl derivatives.

In the light of these recent advances in the area, our motivation in this article is to evaluate the ATRP of methyl methacrylate (MMA) initiated by PHB-Cl as macroinitiator to obtain poly(3-hydroxybutyrate)-*g*-poly(methylmethacrylate) (PHB-*g*-PMMA) brush type graft copolymers.

EXPERIMENTAL

Materials

Carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), methanol (MeOH), tetrahydrofurane (THF), toluene, nitric acid (HNO_3), silicagel, and potassium permanganate ($KMnO_4$) were supplied from Merck and used without purification while only toluene was distilled before use. Hydrochloric acid (HCl) and metallic sodium (Na^0) were purchased from Riedel-de Haen and used as received. 2,2′-bipyridine(bpy), copper(I)bromide (CuBr) were supplied from Aldrich and used as received. Methyl methacrylate (MMA) was supplied from Aldrich and dried over CaH_2 and distilled under vacuum before polymerization.

Synthesis of PHB

Alcaligenes eutrophus (Deutsche Sammlung von Microorganismen und zell kulturen GmbH, DSM no. 428) was grown on saccharose in a 10-L fermenter at 30°C in E-2 medium, and the resulting PHB polymer was extracted in a conventional manner according to the procedures cited in the literature.[4,7,11]

Molecular weight (M_n) and molecular weight distribution (MWD) of PHB was 2.2×10^5 and 3.7, respectively.

Chlorination of the PHB

PHB was partially depolymerized prior to use by heating for 5, 2.5, and 1 h under reflux condenser with 1,2-dichlorobenzene (Merck) to obtain PHB with lower molecular weight (14,852; 77,338; and 93,097 respectively) and thus facilitate solubility and subsequent modifications.

To the $KMnO_4$ crystals placed in a two-necked round bottomed flask, excess HCl was added drop wise to produce chlorine gas. The produced gas was passed through wash bottles containing the concentrated H_2SO_4 and distilled water and then the solution of PHB in $CHCl_3/CCl_4$ (75/25 v/v) in an ice bath under sunlight with a rate that bubbled per second. The solvent was evaporated, and the crude

polymer was washed with methanol and distilled water, respectively, and then dried under vacuum. The gel permeation chromatography (GPC) results, percents of Cl in PHB-Cl (wt %), and initial conditions for the chlorination of PHB were collected in Table I.

Fractional precipitations of PHB-Cl

A dried PHB-Cl was dissolved in specific amount of CHCl$_3$. MeOH was added into the stirring solution of PHB-Cl dropwise until completion of the first precipitation. First fraction of PHB-Cl was separated by decantation and addition of MeOH on the upper solvent of PHB-Cl was continued until precipitation of second fraction. The same procedure was attempted until precipitation ended. γ values were calculated for each fraction as the ratio of the total volume of MeOH used for each fraction to the volume of CHCl$_3$ used for dissolving of PHB-Cl. The fractionated polymers were dried under vacuum and the results were listed in Table I.

Determination of the chlorine content

The determination of the chlorine content in PHB-Cl was performed by the Volhard method as reported previously.[61]

ATRP of methyl methacrylate

ATRP of MMA using PHB-Cl as macroinitiator was carried out following experimental procedure: Macroinitiator (PHB-Cl), ligand (bpy), copper(I)bromide (CuBr), and monomer (MMA) were added to a round-bottom flask sealed with a plastic cap, respectively. Then the flask was sealed and cycled between vacuum and N$_2$ for several times to remove oxygen. After that, the flask was placed in a silicon oil bath at 90°C for 4 h. After a predetermined polymerization time, the polymerization was stopped by exposing to air and diluted with THF. The content was dissolved in THF and subsequently passed through a silica-gel column to remove the ATRP catalyst and the polymer was precipitated from THF into methanol. The product was dried under vacuum at room temperature. The results and conditions of ATRP of MMA were collected in Table II. The polymers were fractionated by fractional precipitation methods and fractional precipitation results were listed in Table III.

Characterization

The ^{1}H-NMR spectra were recorded using Bruker AVANCE-500 spectrometer.

TABLE I
Results and Initial Conditions for the Chlorination of PHB

| Run no. | Initial conditions | | | | | Fractional precipitation | | Cl in PHA-Cl (wt %)[a] | GPC Results | | |
	PHB-I (M_n = 14,852) (g)	PHB-II (M_n = 77,338) (g)	PHB-III (M_n = 93,097) (g)	Cl$_2$ (g)	Yield (g)	γ	wt %		M_n	M_w	MWD
I-1	3	–	–	56.2	2.20	1.1–2.0	46	8.9	5,475	10,587	1.9
I-2	3	–	–	28.0	4.38	0.9–1.4	25	22.4	6,635	10,846	1.6
II-1	–	3	–	56.2	3.17	0.5–2.1	50	8.4	17,418	30,073	1.7
II-2	–	3	–	28.0	5.00	0.7–1.8	63	18.6	7,725	13,060	1.7
II-3	–	3	–	28.0	4.56	0.6–2.3	39	39.8	3,991	11,636	2.9
III-1	–	–	3	56.2	2.27	0.4–1.4	97	2.2	8,682	30,145	3.5
III-2	–	–	3	28.0	3.62	0.3–2.4	51	29.3	2,535	4,039	1.6
III-3[b]	–	–	3	56.2	3.37	0.5–1.9	67	17.0	4,620	7,312	1.6
III-4	–	–	4.5	56.2	6.48	0.4–1.3	73	16.0	5,775	11,234	1.9

[a] Determined by the Volhard method.
[b] Longer chlorination reaction time.

TABLE II
Results and Initial Conditions for Atom Transfer Radical Polymerization of MMA Using Chlorinated PHA as Macroinitiator, Cuprous Bromide (CuBr)/2,2'-Bipyridine Complex as Catalyst, in the Presence of Toluene as Solvent at 90°C

Run no. (PHB-g-PMMA)	PHB-Cl		M_n	t (h)	MMA (mL)	Conv^a (%)	Yield (g)	PHB^b (mol %)	PHB^c (mol %)	$M_{n,th}$	$M_{n,GPC}$	MWD
	Amount (g)	Cl (wt %)										
I-1-1^d	0.51	8.9	5,475	3	2	22.4	0.93	12.0	36	9,955	88,569	1.5
II-1-1^d	1.63	8.4	17,418	2	2	5.3	1.73	16.2	35	18,486	24,927	1.9
II-2-1^d	0.72	18.6	7,725	2	2	20.8	1.11	12.0	37	11,885	9,588	1.3
II-3-1^d	0.75	39.8	3,991	4	4	65.7	3.21	–	42	17,131	21,932	1.7
III-1-1^d	0.81	2.2	8,682	4	2	–	0.30	–	–	–	36,620	1.5
III-2-1^d	0.24	29.3	2,535	4	2	65.7	1.47	–	26	15,675	42,707	1.4
III-3-1^d	0.43	17.0	4,620	4	2	34.2	1.07	–	31	11,460	13,921	1.6
III-1-2^d	0.81	2.2	8,682	4	2	–	0.49	15.7	22	–	59,837	1.5
III-4-1^d	1.08	16.0	5,775	4	4	59.8	3.32	–	33	17,741	11,123	2.2
III-4-2^e	0.73	16.0	5,775	4	4	58.8	2.74	–	22	29,279	21,268	1.4

^{a} Monomer conversion calculated from initial amount of monomer and amount of PMMA in copolymer.
^{b} Percentage of PHB in graft copolymers calculated from ^{1}H-NMR spectra.
^{c} Percentage of PHB in graft copolymers determined from TGA.
^{d} $[M]_o/[I]_o = 200$.
^{e} $[M]_o/[I]_o = 300$ M_n(theoretical) = $[M]_o/[I]_o \times$ %Con. $\times M_w$(monomer) + M_w(initiator). Reaction conditions were determined according to $[I]/[CuBr]/[bpy]$: 1/1/3 and Cl in PHB-Cl (wt %).

The FTIR spectra were recorded using Jasco model 300E FTIR spectrometer.

GPC measurements were conducted with a Knauer GPC in CHCl$_3$ solution at 35°C, at a flow rate of 1 mL/min using ChromGate software, a WellChrom Interface Box, RI Detector K-2301, and WellChrom HPLC pump K-501. Polystyrene standards with low polydispersity obtained from Polyscience were used to generate a calibration curve.

Differential scanning calorimetry (DSC) was carried out on a Setaram DSC 141 with a heating rate 10°C/min under a nitrogen atmosphere.

Thermogravimetric analysis (TGA) was performed on Perkin Elmer Pyris 1 with scan rate of 10°C/min under a nitrogen atmosphere.

Scanning electron microscopy (SEM) analysis was performed using JOEL/JSM-6335F.

RESULTS AND DISCUSSION

The synthesis and characterization of PHB-Cl

PHB-Cl was prepared by passing chlorine gas through PHB solution in CHCl$_3$/CCl$_4$ mixture (75/25 v/v). Results and initial conditions for the chlorination of PHB were listed in Table I. The chlorine contents in chlorinated PHB were changed between 2.18 and 39.8 wt % depending on chlorination reaction time and initial amount of used Cl$_2$ gas. PHB-Cl samples such as I-1 with % 8.9 Cl and II-1 with % 8.4 Cl have randomly monochlorinated repeating units, while samples such as II-3 with % 39.8 Cl and III-2 with % 29.3 Cl have multichlorinated repeating units such as OC(CH$_3$)Cl, CHClCO, and CH$_2$Cl (Table I). In higher chlorinated samples, chlorinated products together with the multichlorinated side chains were formed.[61] It was observed that the molecular weights of chlorinated PHB were lower than that of used PHB for chlorination reactions. This observation attributed to hydrolysis during chlorina-

TABLE III
Fractionation of PHB-g-PMMA Brush Type Graft Copolymers

Run no. (PHB-g-PMMA)	Fractional precipitation results (wt %)			
	$\gamma_{2.8-4.5}$	$\gamma_{4.7-6.9}$	$\gamma_{9.0-9.5}$	$\gamma > 9.5$
I-1-1	100	–	–	–
II-1-1	80	–	–	20
II-2-1	–	45	–	55
II-3-1	–	–	100	–
III-1-2	96	–	–	4
III-2-1	100	–	–	–
III-3-1	100	–	–	–
III-4-1	81	–	–	19
III-4-2	–	96	–	4

γ is 3.0–3.9 for homo-PMMA and γ changes between 0.3 and 2.4 for PHB-Cl.
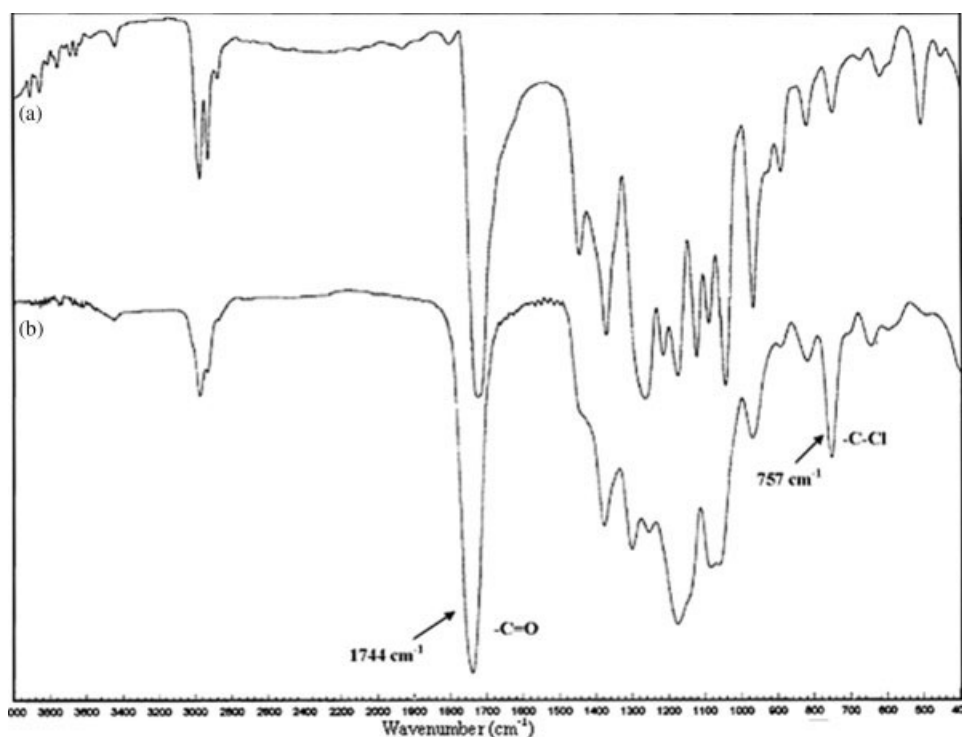
Figure 1 The FTIR spectra of (a) PHB II and (b) PHB-Cl (run no. II-3 in Table I).

tion process. Furthermore decreases in the molecular weights of chlorinated PHB were increased with the increase in chlorine content in PHB (compare run no. II-1, II-2, II-3 in Table I). When run no. III-1 and III-3 which have the same initial conditions in Table I were compared, it was shown that percents of Cl in PHB-Cl were changed from 2.18 to 17.0 wt % by extending the chlorination reaction time, and the molecular weights of PHB-Cl were also decreased from 8682 to 4620 simultaneously. MWDs of the PHB-Cl were extended between 1.6 and 3.5 at a broad range.

The spectroscopic characterization of the chlorinated PHB was performed with FTIR analysis. In the FTIR spectrum of PHB-Cl (run no. II-3 in Table I), the observation of absorption peak corresponding to —C—Cl at 757 cm^{-1} addition to characteristic absorption peaks of PHB confirmed the formation of PHB-Cl structure (Fig. 1).

PHB-*g*-PMMA brush graft copolymers

Brush type PHB-*g*-PMMA graft copolymers with different number of side arm (or density of side chain) were synthesized via ATRP of MMA by using PHB-Cl with different percents of Cl as macroinitiator and cuprous bromide (CuBr)/2,2′-bipyridine complex as catalyst, in the presence of toluene as solvent at 90°C. ATRP of MMA can be initiated by the OC(CH$_3$)Cl, CHClCO, and CH$_2$Cl groups (Scheme 1).

The results and conditions of the polymerizations were collected in Table II. The amounts of CuBr and bpy used were calculated on the basis of [I]/[CuBr]/
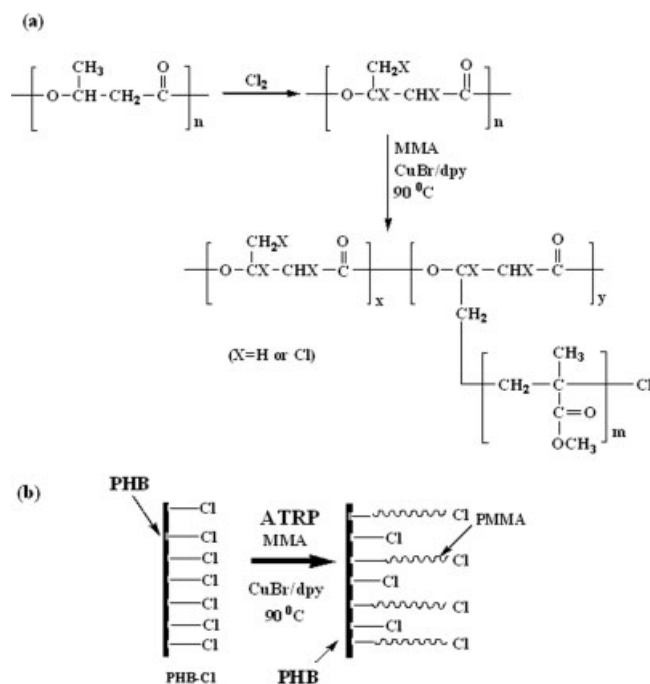
Scheme 1 (a) Chlorination of PHB and the synthesis of PHB-*g*-PMMA brush type graft copolymers by atom transfer radical polymerization of MMA using chlorinated PHB (PHB-Cl) as macroinitiator. (b) Presentation of the synthesis of PHB-*g*-PMMA brushes as schematically.
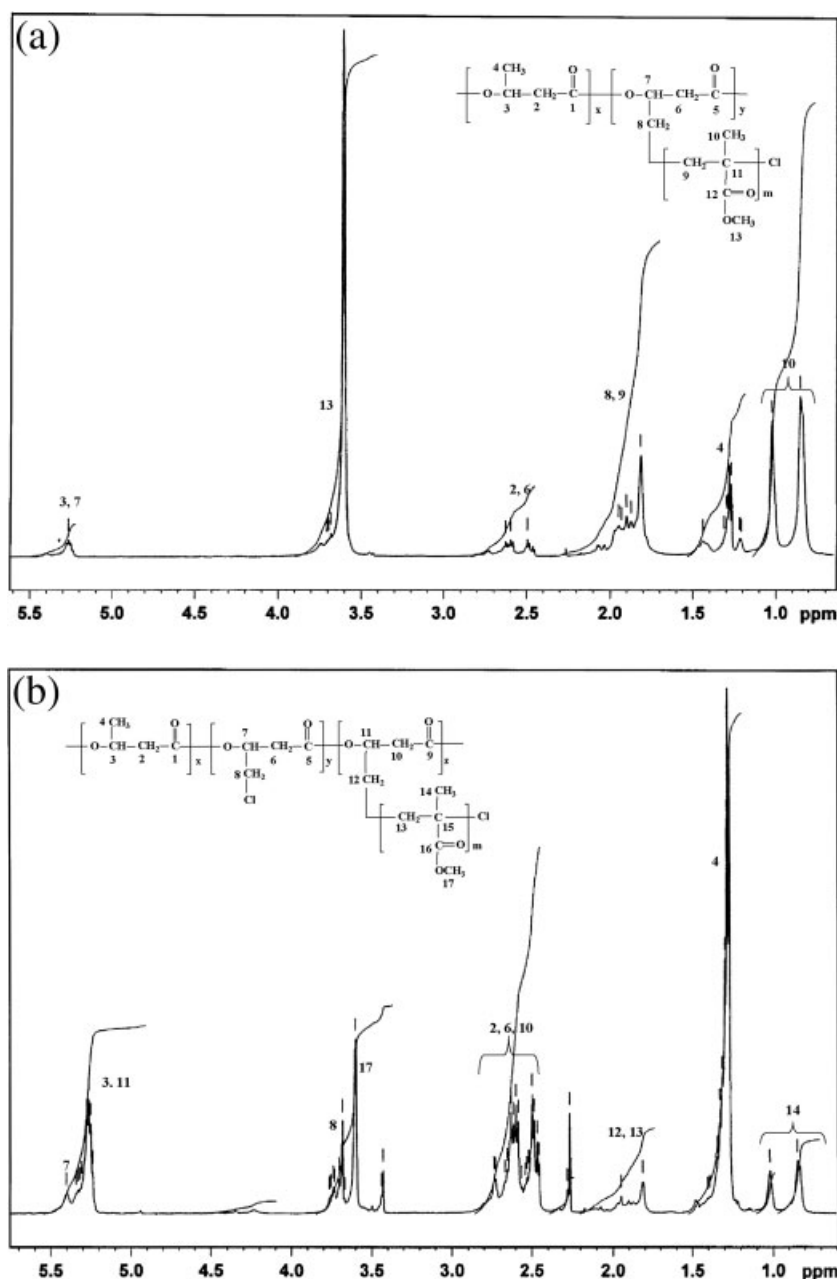
Figure 2 (a) ^{1}H-NMR spectrum of first fraction ($\gamma_{2.8-4.5}$) of PHB-*g*-PMMA brush type graft copolymers (run no. II-1-1 in Table II and Table III); (b) ^{1}H-NMR spectrum of last fraction ($\gamma > 9.5$) of PHB-*g*-PMMA brush type graft copolymers (run no. II-1-1 in Table II and Table III).

[bpy]: 1/1/3 and by considering Cl in PHB-Cl (wt %). Conversion of monomer was increased by extension of polymerization time and reached ~ 66% within 4 h (run no. II-3-1 and III-2-1 in Table II). To attain higher conversion, longer polymerization time is required. Graft copolymers were fractionated by fractional precipitation methods with chloroform as a solvent and methanol as a no solvent. The results of fractional precipitation experiments were listed in Table III. The first fractions of the copolymers were generally used in the characterizations.

The molecular weights of the polymers were determined by GPC analysis and were listed in Table II. GPC results were very important with respect to be first and effective data which established the formation of graft copolymer structure. When the molecular weights of graft copolymers were compared with that of macroinitiators it was observed great increase in the molecular weight of polymers for all experiments, for example, from 5475 for PHB-Cl to 88,569 for PHB-*g*-PMMA (run no. I-1-1 in Table II). At run no. III-4-1 and III-4-2 in the Table II it
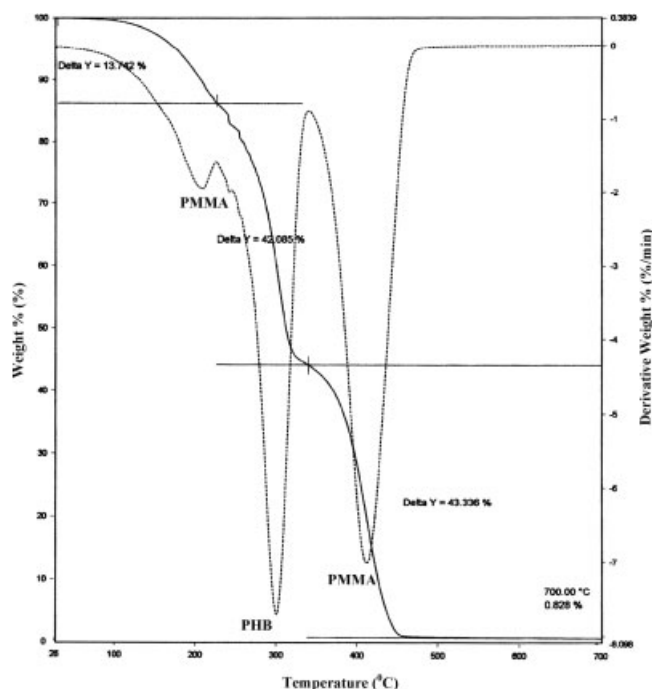
Figure 3 TGA thermogram of PHB-*g*-PMMA brush type graft copolymer (run no. II-3-1 in Table II).

was aimed to change the length of side chain (the molecular weight of PMMA which was as side chain) by varying $[M]_o/[I]_o$ ratio, according to M_n (theoretical) = $[M]_o/[I]_o \times$ %Con. $\times M_w$(monomer) + M_w(initiator) equation. Molecular weight of graft copolymer for run no. III-4-2 with $[M]_o/[I]_o = 300$ was found as 21,268 while for run no. III-4-1 with $[M]_o/[I]_o = 200$ was 11,123. The number average molecular weight of resulting copolymers measured by GPC generally was similar to the theoretical value, but it was not matched with the theoretical value ($M_{n,th} = 11,460$ and $M_{n,GPC} = 13,921$ for run no. II-3-1 in Table II).

The γ values of brush type PHB-*g*-PMMA graft copolymers were ranged from 2.8 to 9.5, depending on PHB and PMMA content in the graft copolymer structure, length of PMMA side chain, molecular weights of graft copolymers, and number of side arm (or density of side chain), but generally brush type PHB-*g*-PMMA graft copolymers precipitated at 2.8–4.5 γ values as expected for typical graft or block copolymers between γ values of related homopolymers while γ values were 0.3–2.4 for PHB-Cl and γ values were 3.0–3.9 for homo-PMMA. Theoretically increase in the number of PMMA side chains of graft copolymers (grafting density) were expected with increase in the percents of Cl in PHB-Cl macroinitiator used and thus decrease in the length of side chain.

The spectroscopic characterization of the polymers was performed with ^{1}H-NMR analysis. Figure 2(a,b)

show the ^{1}H-NMR spectra of first fraction ($\gamma_{2.8–4.5}$) of PHB-*g*-PMMA brush type graft copolymers and second fraction ($\gamma > 9.5$) of PHB-*g*-PMMA brush type graft copolymers (run no. II-1-1 in Table III), respectively. In the ^{1}H-NMR spectrum of first fraction ($\gamma_{2.8–4.5}$) of PHB-*g*-PMMA brush type graft copolymers characteristic peaks for PHB backbone at 1.28 ppm due to —CH$_3$ protons; at 2.5 ppm due to —CH$_2$— protons; at 5.25 ppm due to —CH— proton; and characteristic peaks for PMMA side chains at δ = 1.0–0.8 ppm due to methyl protons (—CH$_3$), at 1.8–2.0 ppm due to methylene protons (—CH$_2$—), at 3.6 ppm due to methoxy protons (—OCH$_3$) were observed [Fig. 2(a)]. Additionally to this peaks in the ^{1}H-NMR spectrum of second fraction ($\gamma > 9.5$) was observed peaks at 3.7–3.8 ppm due to —CH_2—Cl protons and at 5.4 ppm due to —CH—CH$_2$—Cl proton originating from unreacted chlorine in PHB-Cl backbone [Fig. 2(b)].

Thermal characterization of the polymers was performed by using TGA and DSC techniques. TGA thermograms of PHB-*g*-PMMA brush type graft copolymers exhibited three decomposition temperatures (T_d's) at around 210°C for the decomposition of side chains of PMMA together with the residual chloride, which has been lost at broad range at
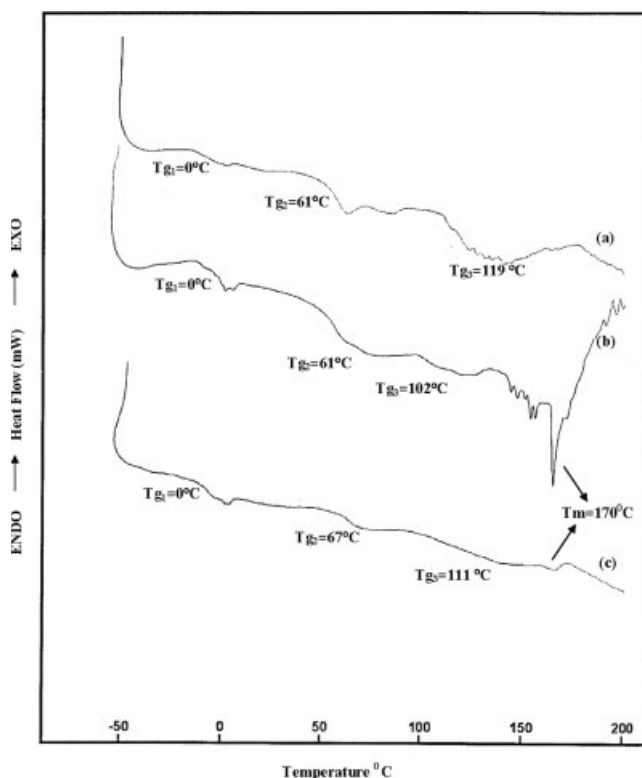

Figure 4 DSC thermograms of PHB-*g*-PMMA brush type graft copolymers (a) run no. II-1-1, (b) run no. II-2-1, and (c) run no. II-3-1 in Table II.
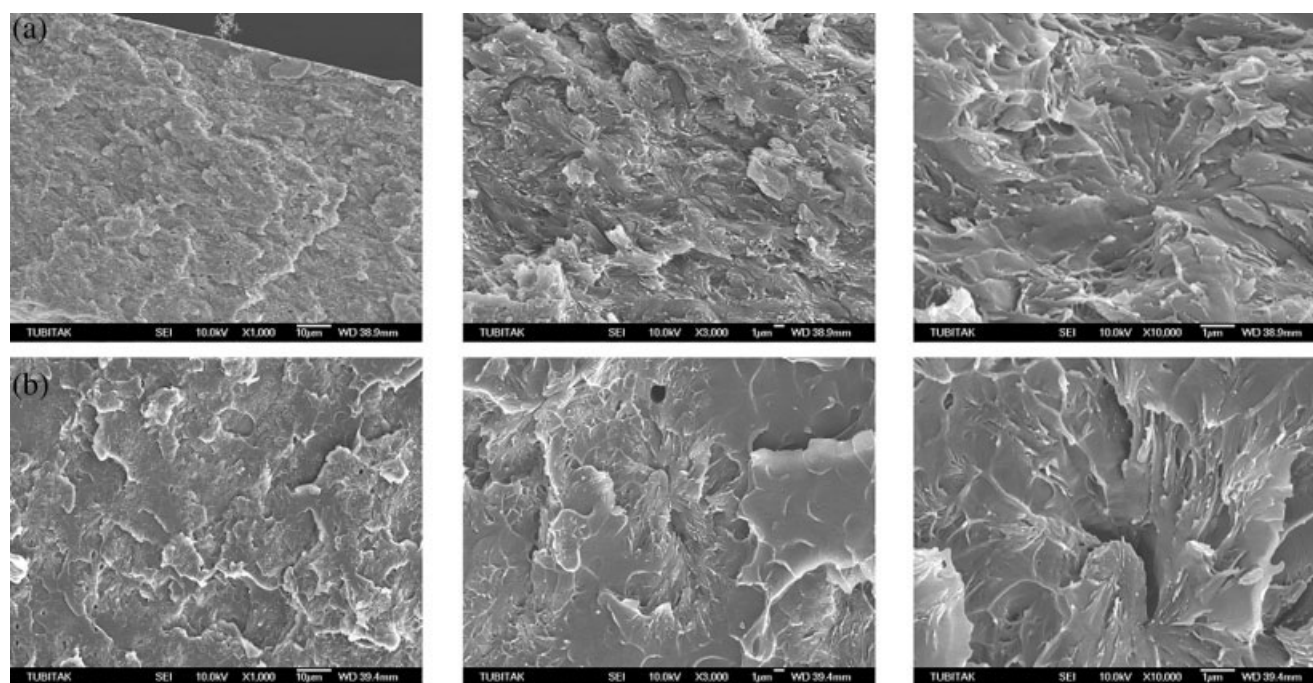
Figure 5 SEM micrographs of (a) PHB-*g*-PMMA brush type graft copolymers run no. III-1-2 in Table II at magnification (×1000), (×3000), and (×10,000); (b) PHB-*g*-PMMA brush type graft copolymers run no. I-1-1 in Table II at magnification (×1000), (×3000), and (×10,000).

around this temperature, at around 410°C for the decomposition of the main chain of PMMA, and at 300°C for decomposition of PHB (Fig. 3). PHB contents of product were determined from TGA thermograms and ranged around 22–42 mol % (Table II). DSC thermogram of PHB-*g*-PMMA brush type graft copolymers generally exhibited three glass transitions at 0°C for PHB segments, around 60°C for miscible parts of PHB-PMMA copolymer domains formed in the graft copolymer structure, which is between their T_{gs} of corresponding homopolymers, around 100°C for PMMA segments, and one melting transition at 170°C for PHB segments (Fig. 4), whereas PHB homopolymers have one T_g between 0 and 4°C, one T_m at 180°C, and PMMA homopolymers have one T_g around 100°C. This finding which is different from glass transition temperatures representing those of corresponding homopolymers is typical for both block and graft copolymers, which have incompatible segments.

The morphologies of PHB-*g*-PMMA brushes were studied by scanning electron microscopy. Figure 5 shows the electron micrographs at three different magnification of PHB-*g*-PMMA brush type graft copolymers films of samples III-1-2 and I-1-1 given in Table II (cast from chloroform) with different PHB content and molecular weight. SEM pictures indicate a continuous polymer matrix with tiny holes around 100 nm. We can attributed the tiny holes to the brush structure.

CONCLUSIONS

An example of further chemical modification of chlorinated PHAs was evaluated. Brush type PHB-*g*-PMMA graft copolymers (cylindrical brush) with narrow MWD were synthesized with "grafting from" technique using PHB-Cl as macro initiator, CuBr/2,2'-bipyridine complex as catalyst, in the presence of toluene as solvent at 90°C by ATRP method. The polymer brushes obtained in this way were fractionated by fractional precipitation methods and the γ values, calculated from the ratio of the volume of nonsolvent to volume of solvent, of brushes were ranged between 2.8 and 9.5 depending on grafting density, side chain length, and molecular weight of brushes. The fractionated brushes were characterized by GPC, ^{1}H-NMR, TGA, and DSC techniques. The morphologies of PHB-*g*-PMMA brushes were also studied by SEM.

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