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Brush Type Copolymers of Poly(3-hydroxybutyrate) and Poly(3-hydroxyoctanoate) with Same Vinyl Monomers via "Grafting From" Technique by Using Atom Transfer Radical Polymerization Method

Hülya Arslan, Nazlı Yeşilyurt, Baki Hazer*

Summary: Brush type graft copolymers of poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxyoctanoate) (PHO) with methylmethacrylate, (MMA), styrene, (S), and n-butylmethacrylate, (n-BuMA) were obtained by using Atom Transfer Radical Polymerization Method, (ATRP), via "grafting from" technique. Firstly PHB and PHO were chlorinated by passing chlorine gas through their solution in $CHCl_3$/CCl_4 (75/25 v/v) mixture and CCl_4, respectively, in order to prepare chlorinated PHB, PHB-Cl, and chlorinated PHO, PHO-Cl, with different chlorine contents. The determination of the chlorine content in chlorinated poly(3-hydroxyalkanoate) (PHA-Cl) was performed by the Volhard Method. Then ATRP of vinyl monomers was initiated by using PHA-Cl as macroinitiators in the presence of cuprous chloride (CuCl)/2,2′-bipyridine complex as catalyst, at 90 °C in order to obtain brushes containing PHAs. The polymer brushes were fractionated by fractional precipitation methods and the γ values calculated from the ratio of the volume of nonsolvent (methanol) and the volume of solvent (chloroform) of brushes varied between 0.82 and 6.50 depending on the composition of brushes. The polymer products were characterized by gel permeation chromatography (GPC), ^{1}H NMR, FTIR, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques.

Keywords: (PHA-*g*-PMMA); atom transfer radical polymerization (ATRP); PHA-Cl macro initiator; poly(3-hydroxyalkanoate)-*graft*-poly(methylmethacrylate); polymer brush

Introduction

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.[1] Because of their branched structure they generally have also 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.).[2] When relatively high grafting density is obtained they are called 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

Department of Chemistry, Zonguldak Karaelmas University, 67100 Zonguldak, Turkey
Fax: +90 372 2574181; E-mail: hulars@yahoo.com

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 and side chains, 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.[3–7] A variety of synthetic methods such as reverse atom transfer radical polymerisation,[8] living anionic surface initiated polymerisation,[9] atom transfer radical polymerization (ATRP),[4,5,10–14] dispersion polymerisation,[15] aqueous atom transfer radical polymerisation,[16] 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.[17–37]

PHAs are highly crystalline, optically active materials that are elaborated by a wide variety of microorganisms as intracellular carbon and energy sources.[38–40] PHAs have many medical and industrial applications because of their biocompatibility, biodegradability and permeability.[41,42] However, some physical and chemical properties, such as low melting transitions causing narrow processability and very high crystallinity causing low solubility and processing problems, mechanical properties and thermal properties, such as thermal instability, have limited their applications. In order to improve the properties of PHAs, chemical modification is a useful technique.[43–45] We have recently reported same new modified polyesters from PHB-Cl and PHO-Cl leading to their corresponding quaternary ammonium salts, sodium sulfate salts, phenyl derivatives.[46,47] PHB-Cl as macroinitiator has also been used in the ATRP of MMA to obtain PHB-*g*-PMMA brush type graft copolymers.[48]

In this study, the synthesis of brush type graft copolymers of PHB and PHO with MMA, S, and n-BuMA was extended to obtain PHA- *g*-PMMA, PHA-*g*-PS and PHA-*g*-P(n-BuMA) via ATRP technique. Then PHO-*g*-PMMA- Cl was used as macroinitiator in the ATRP of MMA and S in order to obtain PHA-*g*-(PMMA-*b*-PMMA) and PHA-*g*-(PMMA-*b*-PS) brush type graft copolymers.

Materials Methods

Materials

Carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), methanol (MeOH), tetrahydrofuran (THF), toluene, nitric acid (HNO_3), silica gel and potassium permanganate ($KMnO_4$) were supplied by Merck and used without purification while only toluene was distilled before use. Hydrochloric acid (HCl) and metallic sodium (Na°) were purchased from Riedel-de Haen and used as received. 2,2′-bipyridine (bpy), copper(I)chloride (CuCl) were supplied from Aldrich and used as received. Methyl methacrylate (MMA), styrene (S) and n-butyl methacrylate (n-BuMA) were supplied by Aldrich and dried over CaH_2 and distilled under vacuum before polymerization.

Synthesis of PHAs

PHB and PHO produced by *Alcaligenes eutrophus* and *Pseudomonas oleovorans*, respectively, according to the procedures cited in the literature,[49,50] were supplied by TUBITAK-MAM (Gebze-Kocaeli, TURKEY).

Chlorination of the PHAs

PHB and PHO were chlorinated by passing chlorine gas through their solution in $CHCl_3/CCl_4$ (75/25 v/v) mixture and CCl_4, respectively, in order to prepare chlorinated PHB, PHB-Cl, and chlorinated PHO, PHO-Cl, with different chlorine contents. The determination of the chlorine content in PHA-Cl was performed by the Volhard Method as reported previously.[48] The GPC results, amount of Cl in PHA-Cl (% w/w), initial conditions for the chlorination of PHAs are presented in Table 1.

ATRP of Vinyl Monomers using PHB-Cl and PHO-Cl as Macroinitiator

ATRP of MMA, S and n-BuMA were carried out following the experimental procedure below. Macroinitiator (PHA-Cl), ligand (bpy), copper(I)chloride (CuCl) and monomer 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 in order to remove oxygen. After that, the flask was placed in a silicon oil bath at 90 °C. After a predetermined polymerization time, the reaction 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 or petroleum ether. The product was dried under vacuum at room temperature.

ATRP of MMA and S using PHO-*g*-PMMA-Cl Brush Type Graft Copolymers as Macroinitiator

ATRP of MMA and S using PHO-*g*-PMMA-Cl brushes as macroinitiator were performed with same experimental procedure.

Instrumentation

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

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

GPC measurements were conducted with a Knauer gel permeation chromatography 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 Polysciences were used to generate a calibration curve.

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

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) were performed on Perkin Elmer Pyris 1 with scan rate of 10 °C/min. under a nitrogen atmosphere.

Scanning Electron Microscopy (SEM) Analysis were performed using JOEL/JSM-6335F.

Table 1.
Synthesis of macroinitiators (PHB-Cl and PHO-Cl) for ATRP of the vinyl monomers.

Run No	Initial Conditions				Yield (g)	Cl in PHA-Cl % w/w[a)]	GPC Results	
	PHB-IV (M_n 70,805) (g)	PHO-I (M_n 1,869,534) (g)	PHO-II (M_n 151,173) (g)	Cl_2 (g)			M_n	MWD
IV-I	4.5			56.0	7.9	7.3	19850	1.9
IV-2	4.6			56.0	6.6	9.9	4758	2.2
I-1		4.1		56.0	9.7	25.4	29454	1.9
I-2		4.5		56.0	10.9	11.9	64593	2.1
II-2			3.0	56.0	5.9	18.3	32219	2.8

a)Determined by the Volhard Method.

Results and Discussion

The Synthesis and Characterization of PHB-Cl and PHO-Cl

PHB-Cl and PHO-Cl were prepared by passing chlorine gas through PHAs solution in $CHCl_3/CCl_4$ (75/25 v/v) mixture and CCl_4, respectively. Results and initial conditions for the chlorination reaction were listed in Table 1.

The chlorine contents in chlorinated PHAs were changed between 7.3 and 25.4 wt %. PHA-Cl samples such as IV-1, IV-2 and I-2 with lower chlorine contents have randomly monochlorinated repeating units, while samples such as I-1 and II-2 with higher chlorine contents have multichlorinated repeating units (Table 1).[48]

PHA-Cl samples were fractionated by fractional precipitation method to obtain chlorinated polymers of higher molecular weight and γ values, the solvent/nonsolvent ratio, ranged between 0.04 and 2.33 at broad range were calculated. It was observed that the molecular weights of the first fraction of chlorinated PHA were lower than that of used PHA for chlorination reactions. This observation can be attributed to hydrolysis during chlorination process. Furthermore decreases in the molecular weights of chlorinated PHA were increased with the increase in chlorine content in PHA. When run no I-1 and I-2 which have the same initial conditions in Table 1 were compared it was shown that percents of Cl in PHO-Cl were changed from 11.9 wt % to 25.4 wt % and the molecular weights of PHO-Cl were also decreased from 64593 to 29454 simultaneously. Molecular weight distributions of the PHB-Cl and PHO-Cl ranged between 1.9–2.8.

The spectroscopic characterization of the chlorinated PHA was performed with FTIR and ^1H NMR analysis. In the FTIR spectrum of PHA-Cl the observation of absorption peak corresponding to –C–Cl at 757 cm^{-1} addition to characteristic absorption peaks of PHA confirmed the formation of PHA-Cl structure.[48] The ^1H-NMR spectra of chlorinated PHO samples showed differences depending on the chlorine content. Firstly it is observed that signals of methylene ($-CH_2-$) and methyl ($-CH_3$) groups shifted to lower fields in the ^1H NMR spectra (Figure 1). In the ^1H NMR spectrum of PHO-Cl (Run no I-1 with 25.40 wt % Cl) signals at 1.5–1.6 ppm for terminal methyl ($-CH_3$) groups, at 1.8 ppm for methylene ($-CH_2-$) groups of the side chain of polymer, at 2.3 ppm for methylene ($-CH_2-$) group connecting to β-carbon of main chain of polymer were observed. Signals for α-protons and β-protons of main chain were also shifted to 2.9 ppm and 5.5 ppm respectively due to the electron-withdrawing effect of neighbouring chlorine atoms. ($-CH_2Cl$) signals at 3.9 ppm and ($-CHCl-$) signals between 4.1–4.7 ppm were observed. Polychlorinated sample I-1 has also a signal corresponding to terminal ($-CHCl_2$) groups at 6 ppm.

The Synthesis and Characterization of Brushes

PHA-g-PMMA, PHA-g-PS and PHA-g-PnBMA brush type graft copolymers with different number of sidearm were synthesized *via* ATRP of MMA, S and nBuMA, respectively, using PHA-Cl with different amounts of Cl as macroinitiator and cuprous bromide /2,2′-bipyridine complex as catalyst, in the presence of toluene as solvent at 90 °C (in the case of styrene at 100 °C) (Scheme 1). The results and conditions of the polymerizations were collected in Table 2.

The amounts of CuBr and bpy used were calculated on the basis of [I]/[CuBr]/[bpy]: 1/1/3 and by considering Cl in PHB-Cl (wt %) as described previously. Yields are generally low and are not affected by the extension of polymerization time (extension of polymerization time does not affect the yield of polymerizations).

Generally dark brown products were obtained and analysed by UV-Vis spectroscopy. In the UV-Vis spectrum of graft copolymer (Run no I-1-2) no absorption peaks were observed corresponding to copper salts (CuCl and/or $CuCl_2$), ligand and CuCl/2,2′-Bipyridine complex.

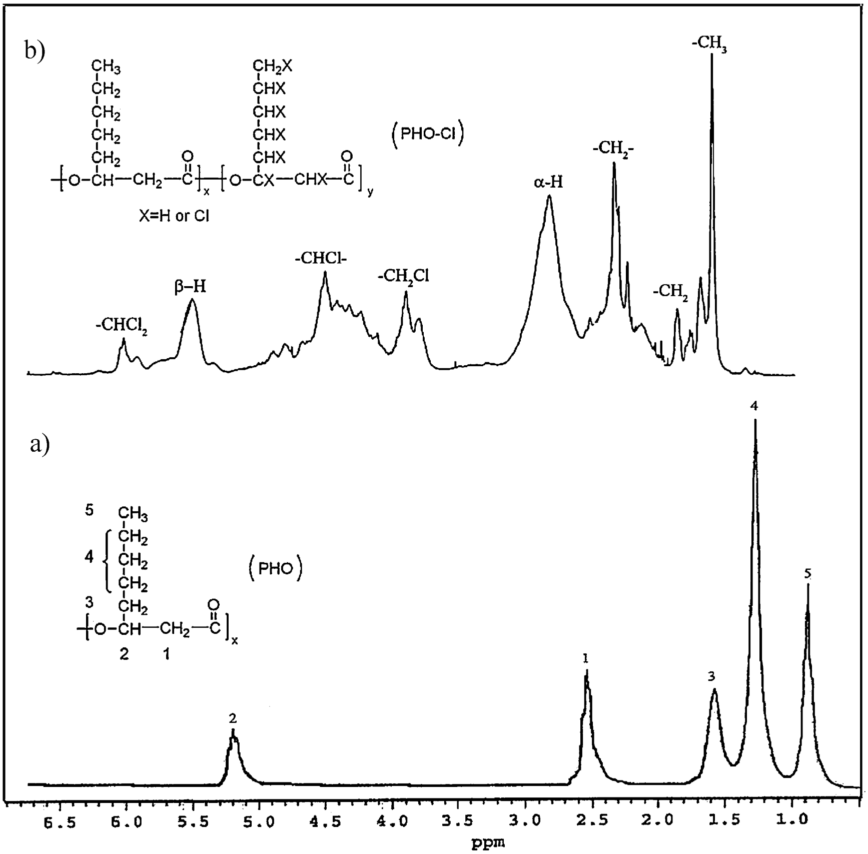
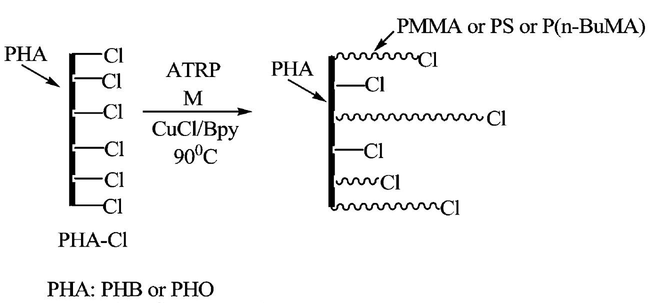


Figure 1.
^{1}H-NMR spectra of (a) PHO and (b) PHO-Cl (Run No.I-1 in Table 1).

Graft copolymers were fractionated by fractional precipitation methods with chloroform as a solvent and methanol as a nonsolvent. The results of fractional precipitation experiments were listed in Table 3. The first fractions of the copolymers were generally used in the characterizations. The γ values of graft copolymers were ranged from 0.82 to 6.50 depending on composition of brushes as expected for



Scheme 1.
The synthesis of PHA-*g*-PMMA, PHA-*g*-PS and PHA-*g*-PBMA brush type graft copolymers.

Table 2.
Results and initial conditions for ATRP of MMA, S and n-BuMA using chlorinated PHA as macroinitiator, cuprous chloride/2,2′-bipyridine complex as catalyst.

Run No	PHB-Cl			PHO-Cl			t (h)	MMA (mL)	S (mL)	n-BuMA (mL)	Yield (g)	$M_{n,GPC}$	MWD
	Amount (g)	Cl (% w/w)	M_n	Amount (g)	Cl (% w/w)	M_n							
IV-1-2	1.7	7.3	19850	–	–	–	20	–	2	–	0.5	1255	1.6
IV-1-3	1.2	7.3	19850	–	–	–	4	–	–	2	1.2	8912	1.5
IV-2-1	0.3	9.9	4758				7			2	1.6	30889	1.6
I-1-1				2.7	25.4	29454	4	2	–	–	3.1	4541	3.1
(I-1-1)t				2.7	25.4	29454	4	2	–	–	3.5	5017	3.5
I-2-1				4.4	11.9	64593	8	1.5	–	–	1.9	1570	2.5
II-2-2				2.8	18.3	32219	20	–	2	–	1.6	3070	2.3
II-2-3				2.0	18.3	32219	20	–	–	2	0.8	7712	1.9

$[M]_o/[I]_o = 200$ $M_n(\text{theoretical}) = [M]_o/[I]_o \times \%\text{Con.} \times M_w(\text{monomer}) + M_w(\text{initiator})$
Reaction conditions were determined according to [I]/[CuBr]/[bpy]: 1/1/3 and Cl in PHA-Cl (wt %)

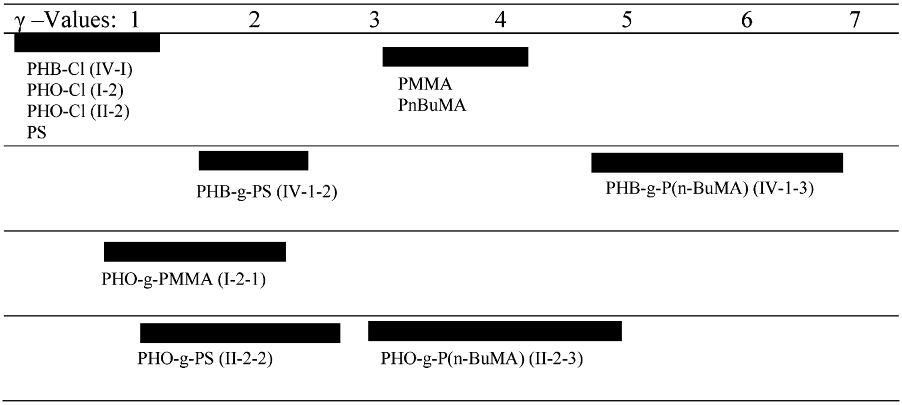
typical graft or block copolymers between γ values of related homopolymers while γ values were 0.04–1.07 for PHA-Cl, 3.0–3.9 for homo-PMMA, 0.4–0.9 for PS and 2.8–4.1 for PnBuMA.

The molecular weights of the polymers were determined by GPC analysis and were listed in Table 2. It was observed that the molecular weights of graft copolymers were lower than that of corresponding PHA-Cl used as macroinitiator. This observation can be attributed to hydrolysis of PHA backbone during ATRP process.

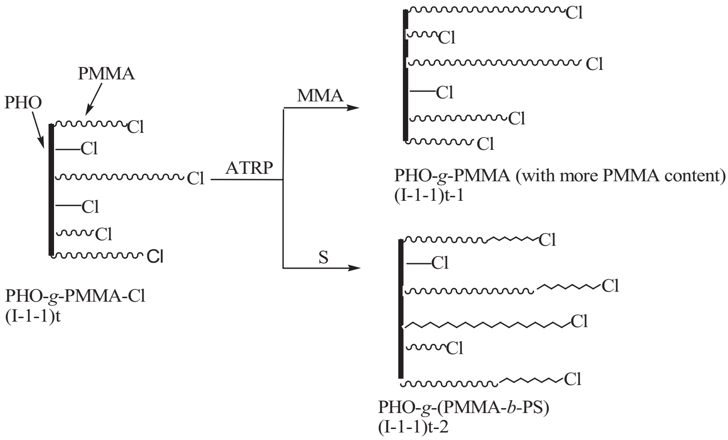
PHO-*g*-PMMA (with more PMMA content) and PHO-*g*-(PMMA-*b*-PS) brush type graft copolymers were also synthesized via ATRP of MMA and S using PHO-g-PMMA-Cl as macroinitiator (Scheme 2) in order to obtain colorless and flexible (not brittle) products. The results and conditions of the polymerizations were collected in Table 4. Creamy and less brittle products were obtained.

The spectroscopic characterization of the polymers was also performed with ^{1}H NMR analysis. Figure 2(b) show the ^{1}H NMR spectra of PHB-*g*-PnBuMA graft copolymers (Run no IV-1-3 in Table 2). In the ^{1}H NMR spectrum of PHB-*g*-PnBuMA brush type graft copolymers characteristic peaks for PHB backbone at $\delta = 1.28$ ppm due to $-CH_3$ protons; at 2.8–3.0 ppm due to $-CH_2-$ protons and at 5.4 ppm due to –CH– proton (shifted to higher field due to the

Table 3.
Schematic presentation of variation of γ –values of polymers depending on composition of the brushes.



Solvent: Chloroform, Nonsolvent: Methanol



Scheme 2.
The synthesis of PHO-*g*-(PMMA-*b*-PS) brush type graft copolymers.

electron-withdrawing effect of neighbouring chlorine atoms) and characteristic peaks for PnBuMA side chains at $\delta = 1.0$–0.8 ppm due to methyl protons ($-CH_3$), at 1.3–1.6 ppm due to methylene protons ($-CH_2-$)of side chains, at 1.8–2.0 ppm due to methylene protons ($-CH_2-$) of main chain, at 3.94 ppm due to the ester methylene proton ($-COOCH_2-$) in the PnBMA units were observed (Figure 2(b)). In addition to these, peaks at 3.7 ppm due to $-\underline{CH_2}-Cl$ protons and at 5.5–5.6 ppm due to $-\underline{CH}-CH_2-Cl$ proton originating from unreacted chlorine in PHB-Cl backbone (Figure 2 (b)) were observed.

Figure 3(b) and 3(c) show the ^{1}H NMR spectra of PHO-*g*-PMMA graft copolymers (Run no (I-1-1)t in Table 2) and PHO-*g*-(PMMA-*b*-PS) graft copolymers (Run no (I-1-1)t-2 in Table 4) respectively. In the ^{1}H NMR spectra of PHO-*g*-PMMA graft copolymers characteristic peaks for PMMA side chains at $\delta = 1.0$–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 in addition to characteristic peaks of PHO-Cl backbone. The ^{1}H NMR spectra of PHO-*g*-(PMMA-*b*-PS) graft copolymers revealed the characteristic peaks for PS blocks at $\delta = 6.6$–7.1 ppm due to aromatic protons, in addition to ^{1}H NMR spectra of PHO-*g*-PMMA graft copolymers.

Thermal characterization of the polymers was performed by using TGA and DSC techniques. Table 5 lists the glass transition (T_g), melting transition (T_m) and decomposition (T_d) temperatures of graft copolymers. Thermal analysis results confirmed the formation of graft copolymer structure.

Differential thermogravimetry (DTG) thermograms of PHO-*g*-PMMA brush type graft copolymers (Run no (I-1-1)t)

Table 4.
Results and initial conditions for atom transfer radical polymerization of MMA and S using PHO-*g*-PMMA-Cl brush type graft copolymers as macroinitiator, cuprous chloride/2,2′-bipyridine complex as catalyst.

Run No	PHO-*g*-PMMA-Cl			t (h)	MMA (mL)	S (mL)	Yield (g)	$M_{n,GPC}$	MWD
	Amount (g)	Cl (% w/w)	M_n						
(I-1-1)t-1	0.46	15	5017	4	2	–	1.37	17698	1.34
(I-1-1)t-2	0.44	15	5017	6	–	2	0.53	2940	1.19

$[M]_o/[I]_o = 200$ $M_n(\text{theoretical}) = [M]_o/[I]_o \times \%\text{Con.} \times M_w(\text{monomer}) + M_w(\text{initiator})$.

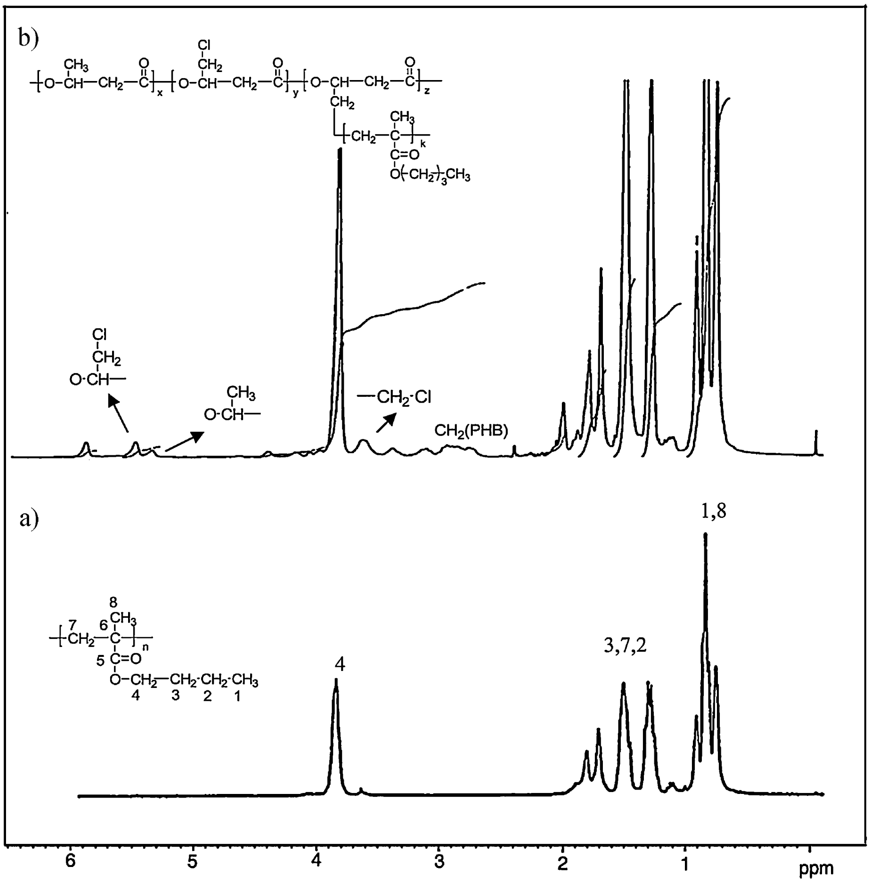


Figure 2.
^{1}H-NMR spectra of (a) PnBMA, (b) PHB-*g*-PnBMA (Run no (IV-1-3) in Table 2).

exhibited three decomposition temperatures (T_d) at around 250 °C for the decomposition of side chains of PMMA together with the residual chloride which has been lost at broad range at around this temperature, at around 410 °C for the decomposition of the main chain of PMMA and at 270 °C for decomposition of PHO while PHO-Cl (Run no (I-1)) has decomposition temperature at 270 °C (see Figure 4 (a) and Figure 4 (b)). In the DTG thermogram of PHO-*g*-PMMA (with more PMMA content) (Run no (I-1-1)t-1) it can easily be seen that insertion of more MMA to the graft copolymer structure because of increase in volume of peak at 400 °C corresponding to the decomposition of the main chain of PMMA (Figure 4 (c)). DTG thermograms of PHO-*g*-(PMMA-*b*-PS) brush type graft copolymers (Run no (I-1-1)t-2) also exhibited three decomposition temperatures (T_d's) at around 200 °C for the decomposition of side chains of PMMA, at around 400 °C for the decompositions of the main chain of PMMA and PS, and at 275 °C for decomposition of PHO (Figure 4 (d)). These results demonstrated that ATRP mechanism in Scheme 2 proceeded successfully.

DSC curve of PHO (I) exhibited one sharp and strong melting transition at 49.5 °C and one exotherm around 210 °C. In the DSC curve of PHO-Cl (Run no (I-1) in Table 1) one sharp and slight melting transition at 71 °C was observed because of destruction of crystalline structure of PHO

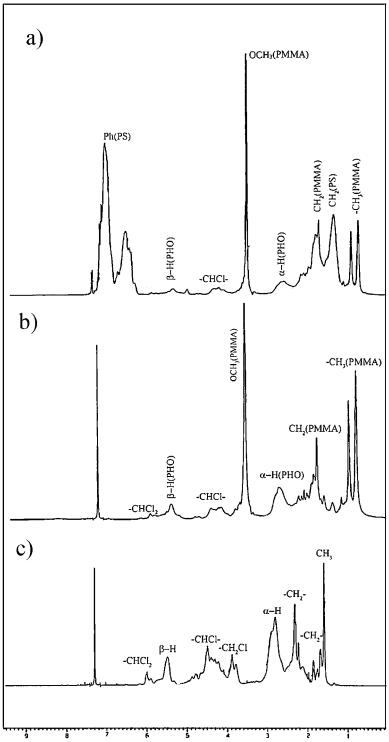


Figure 3.
^{1}H-NMR spectra of (a) PHO-Cl (Run no. I-1 in Table 1), (b) PHO-*g*-PMMA (Run no (I-1-1)t in Table 2), (c) PHO-*g*-(PMMA-*b*-PS) (Run no (I-1-1)t-2 in Table 4).

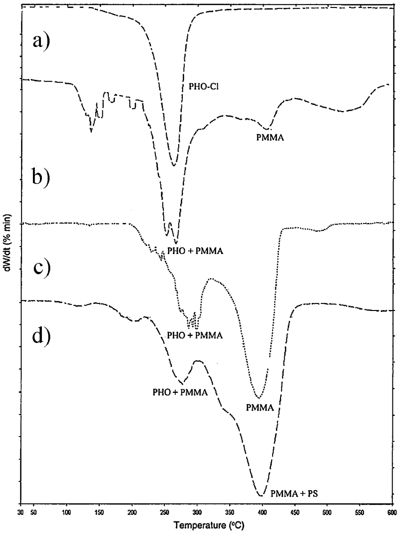


Figure 4.
DTG thermograms of (a) PHO-Cl (Run no. I-1 in Table 1), (b) PHO-*g*-PMMA (Run no (I-1-1)t in Table 2), (c) PHO-*g*-PMMA with higher PMMA content (Run no (I-1-1)t-1 in Table 4), (d) PHO-*g*-(PMMA-*b*-PS) (Run no (I-1-1)t-2 in Table 4).

by chlorination reactions, and another exotherm around 250 °C. DSC thermogram of PHO-*g*-PMMA graft copolymers (Run no (I-1-1)t in Table 2) exhibited one melting transition at 46 °C for PHO segments (in fact, PHO has T_m at around 65 °C, [50]), one glass transition around 110 °C for PMMA segments and one glass transition at around 40 °C due to miscible blends of PHO-g-PMMA (Figure 5 (c)). In the case of PHO-*g*-PMMA graft copolymers (with more PMMA content) (Run no (I-1-1)t-1 in Table 4) it was observed only one glass transition at 117 °C for PMMA segments because of insertion of more PMMA into graft copolymer structure and thus destruction of all crystalline structure of PHO (Figure 5 (d)). In the DSC thermogram of PHO-*g*-(PMMA-*b*-PS) graft copolymer (Run no (I-1-1)t-2 in Table 4) one glass transition was observed at around 60 °C for

Table 5.
Thermal analysis of the graft copolymers.

Run No	DSC				TGA		
	Tg1	Tg2	Tm1	Tm2	Td1	Td2	Td3
PHO-g-PMMA (I-1-1)t	40	110	46	–	250	265	405
PHO-g-PMMA (I-1-1)t-1	–	117	226	–	–	280	400
PHO-g-PMMA-b-PS (I-1-1)t-2	60	–	66	–	205	275	400
PHB-g-PS (IV-1-2)			76		235	375	700–900
PHB-g-PBMA (IV-1-3)	25				240	285	410
PHO-g-PS (II-2-2)			48	255		270	450
PHO-g-PBMA (II-2-3)			53	251	270	350	500–700
PHO-g-PMMA (I-1-1)t		110	46	251	255	270	415

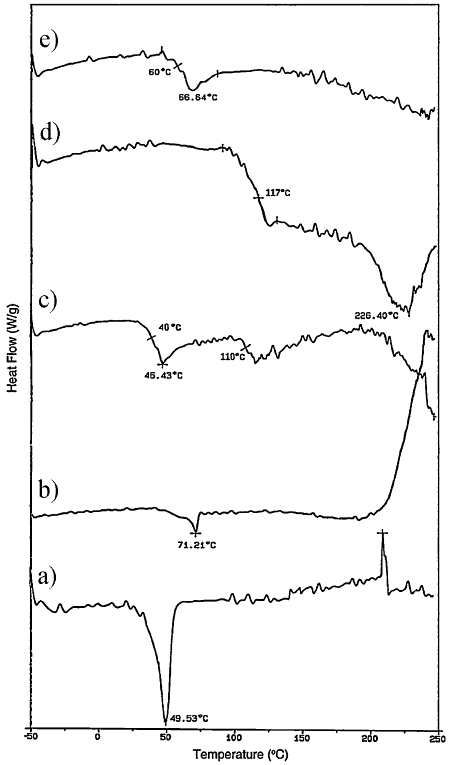


Figure 5.
DSC thermograms of (a) PHO (I), (b) PHO-Cl (Run no. I-1 in Table 1), (c) PHO-*g*-PMMA (Run no (I-1-1)t in Table 2), (d) PHO-*g*-PMMA (Run no (I-1-1)t-1 in Table 4), (e) PHO-*g*-(PMMA-*b*-PS) (Run no (I-1-1)t-2 in Table 4).

miscible blends of PHO-g-(PMMA-b-PS) and one melting transition at around 66 °C for PHO segments (Figure 5 (e)). Insertion of PS into graft copolymer structure did not destroy crystalline structure of PHO as that of PMMA.

Conclusion

Halogenated PHAs as macroinitiators can be used in ATRP of vinyl monomers to obtain brush type multi-graft copolymers. PHA-*g*-PMMA, PHA-*g*-PS and PHA-*g*-PnBMA brush type graft copolymers with different number of side arms were synthesized *via* ATRP of MMA, S and nBuMA, respectively, using PHA-Cl with different percents of Cl as macroinitiator and cuprous chloride (CuCl)/2,2′-bipyridine complex as catalyst at 90 °C (in the case of styrene at 100 °C). Using PHO-*g*-PMMA-Cl as macroinitiator PHO-*g*-(PMMA-*b*-PS) brush type graft copolymers can also be synthesized *via* ATRP of S. Furthermore during this process, chain scission of the microbial polyester was unavoidable. The polymer brushes obtained in this way were fractionated by fractional precipitation methods and the γ values of brushes, calculated from the ratio of the volume of nonsolvent to volume of solvent, ranged between 0.82 and 6.50 depending on the composition of brushes. These multigraft brush copolymers can be promising materials for industrial and medical applications because they contain biodegradable PHA units in the copolymer structure.

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