# The Synthesis of PHA-*g*-(PTHF-*b*-PMMA) Multiblock/ Graft Copolymers by Combination of Cationic and Radical Polymerization

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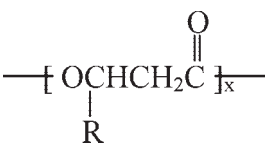
**ABSTRACT:** A new and promising method for the diversification of microbial polyesters based on chemical modifications is introduced. Poly(3-hydroxy alkanoate)-*g*-(poly(tetrahydrofuran)-*b*-poly(methyl methacrylate)) (PHA-*g*-(PTHF-*b*-PMMA)) multigraft copolymers were synthesized by the combination of cationic and free radical polymerization. PHA-*g*-PTHF graft copolymer was obtained by the cationic polymerization of THF initiated by the carbonium cations generated from the chlorinated PHAs, poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx) in the presence of $AgSbF_6$. Therefore, PHA-*g*-PTHF graft copolymers with hydroxyl ends were produced. In the presence of $Ce^{+4}$ salt, these hydroxyl ends of the graft copolymer can initiate the redox polymerization of MMA to obtain PHA-*g*-(PTHF-*b*-PMMA) multigraft copolymer. Polymers obtained were purified by fractional precipitation. In this manner, their $\gamma$-values (volume ratio of nonsolvent to the solvent) were also determined. Their molecular weights were determined by GPC technique. The structures were elucidated using $^1$H-NMR and FTIR spectroscopy. Thermal analyses of the products were carried out using differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2308–2317, 2009

**Key words:** poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV); poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBHx); bacterial polyesters; polytetrahydrofuran (PTHF); poly(methyl methacrylate) (PMMA); block and graft copolymers

## INTRODUCTION

Poly(3-hydroxyalkanoate)s (PHAs) are originally natural aliphatic polyesters, which are distributed in biological systems and are produced within the cytoplasm of many prokaryotic organisms as intracellular carbon and energy sources.[1–4] By feeding bacteria with specific and unusual carbon compounds, it is possible to induce bacteria to produce polymers that are not usually produced in nature.



In this structure, R is an alkyl side chain of naturally occurring 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, sclPHA with an alkyl side chain having 1 to 2 carbon, produced by various bacteria, including *Alcaligenes eutrophus* (renamed *Ralstonia eutropha*, more recently changed again *Wautersia eutropha*[1]) or a medium-chain-length, mclPHA with an alkyl side chain consisting of more than or equal to 3 carbon atoms, produced, for example, by *Pseudomonas oleovorans*.[4] The most well-known member of the sclPHAs, PHB is a 100% biodegradable and biocompatible polymer with the glass transition temperature ($T_g$) of 0–10°C, the melting temperature ($T_m$) of 175–180°C, and the degradation temperature ($T_d$) of 252°C. It is also a water- and moisture-resistant thermoplastic polymer.[2,3] However, its highly crystalline and brittle structure, low impact strength, and nearly insoluble nature bring about shortcomings to use PHB in medical, pharmaceutical, and industrial areas. To improve the physical and chemical properties of PHB, there have been a lot of attempts to incorporate

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various functional groups, different repeating units into the PHB structure by means of both biosynthetic and chemical modification processes.[5–9] Valerate and hexanoate copolymers of PHB, PHBV, and PHBHx, which are obtained by the biosynthetic modification, are much ductile elastomeric biodegradable polyesters and easily processible like commercial polyolefins for industrial applications.[10–14]

To insert a different polymer segment into a polymer segment is important for obtaining new materials such as block and graft copolymers. A variety of synthetic methods for the preparation of block/graft copolymers with various architectures such as linear diblock (AB), triblock (ABA or ABC), pentablock (ABABA), multiblock or segmented copolymers have been proposed.[15–32] In this manner, transformation reactions to polymer anion,[33–38] cation to radical transformation reactions,[39–42] and polymer anion to polymer cation[43,44] were successfully used to prepare block/graft copolymers. Among these methods, the cation to radical transformation reactions are generally based on preparing poly-THF having peroxidic or azo groups[45–50] to insert PTHF blocks in the copolymer structure, which enhance the flexibility and thermoplasticity of the copolymer. The soft poly-THF blocks enhance the flexibility and thermoplasticity of the copolymer.

The insertion of PMMA units, which is an important commercially available polymer and has many industrial and medical applications especially because of its excellent optic properties into biodegradable polymers (PHAs and PTHF), is also important for chemical modification reactions of biodegradable polymers.

Chlorinated PHB (PHB-Cl)/PMMA blends were also obtained and the mechano-optical behavior of blend films was investigated.[51]

This work refers to a novel and promising method of extending of the diversity of the microbial polyesters via cation to radical transformation reactions leading to PHA-*g*-(PTHF-*b*-PMMA) multigraft copolymer. In this study, it is aimed the synthesis of multiblock copolymers of PHAs with PTHF and PMMA due to modifying the flexibility, thermoplasticity and film properties.

## EXPERIMENTAL

### Materials

PHB-*co*-10 mol % HV copolymer (PHBV) was prepared from *A. eutrophus* grown on linseed oil according to the procedures cited in the reference.[52] PHBHx (12 mol % HHx) was received from the Procter & Gamble Company (USA).

THF was refluxed over Na-metal, distilled, and middle fraction was taken just before use. Acetonitrile was distilled on $CaH_2$, middle fraction was used for solution cationic polymerization of THF. MMA was freed from inhibitor using 10 wt % NaOH solution, dried on anhydrous sodium sulfate, and then distilled on $CaH_2$. Other chemicals and organic solvents used in this study were purchased from Aldrich and used as received.

### Thermal degradation of PHBV

Bacterial PHBV (10 g) was refluxed in 1,2-dichlorobenzene (50 mL) for the periods of time. Afterward, the reaction medium was quickly cooled to the room temperature, the solvent was evaporated; degraded PHBV residue was precipitated from methanol and dried under vacuum at room temperature.

### Chlorination of the PHAs

The chlorination procedure was performed according to the procedure cited in reference.[53,54] As an example for the procedure, to the $KMnO_4$ crystals placed in a two-necked round-bottomed flask, excess HCl was added dropwise to produce chlorine gas (1 g of chlorine gas needs 0.89 g of $KMnO_4$). Required moles of the produced gas were passed, at a bubble per second, through water, concentrated $H_2SO_4$, an empty wash bottle, and then a solution of PHA in $CHCl_3/CCl_4$ (75/25 v/v) in an ice bath under sunlight. The solvent was evaporated, and the crude polymer was washed with MeOH, dried under vacuum, and then fractionally precipitated. The precipitated polymer fractions were dried under vacuum at room temperature.

### Fractional precipitations of PHA-Cl

Fractional precipitations of PHA-Cl were carried out according to the procedure cited in the literature.[25] Vacuum-dried chlorinated biopolyester sample was dissolved in 5 mL of $CHCl_3$. To the stirring solution, MeOH was added dropwise until completion of the first precipitation. After decantation, the upper solvent was followed by the addition of MeOH for the second fraction. The same procedure was attempted until no more precipitation. Gamma ($\gamma$) values were calculated as the ratio of the total volume of MeOH used for each fraction to the volume of $CHCl_3$. Polymer fractions were dried under vacuum.

### Determination of chlorine content by the Volhard method

Chlorinated polymer (50 mg) was fusioned with 30 mg of $Na^0$ to transform Cl to NaCl. To the reaction

content was added 2 mL of distilled water, and then the mixture was acidified with dilute $HNO_3$. Afterward, analytical content of NaCl was determined by the titration of standard solution of $AgNO_3$ via the Volhard method.[55]

### THF polymerization initiated by the $AgSbF_6$ + PHA-Cl catalyst system

A given amount of PHA-Cl and $AgSbF_6$ initiator system and THF were placed into the three-necked round bottom flask (250 mL) attached a reflux condenser, a thermometer, and a gas inlet syringe. Argon was purged into the solution for 1 min to expel the air. THF polymerization was initiated by the catalyst system in bulk or in acetonitrile solution at 30 or 40°C. After a given polymerization time, polymer precipitated into 1 L $10^{-3}$ M $NH_3$ solution. Polymer precipitated was dried under vacuum, redissolved in THF, filtered from AgCl residue, and reprecipitated in water to purify the copolymer.

### Polymerization of MMA by ($Ce^{+4}$/-diol redox system) initiated by (PHA-*g*-PTHF) graft copolymers

Using the same procedure reported in the reference,[56] the PHA-*g*-PTHF graft copolymers with hydroxyl ends and Ce(IV)-salt redox system initiated to the polymerization of MMA to obtain PHA-*g*-(PTHF-*b*-PMMA) multigraft/block copolymer.

### Characterization of the polymers

$^1$H-NMR spectra of the products were recorded using a Bruker AVANCE-500 NMR spectrometer, in $CDCl_3$ solvent. FTIR spectra were recorded of the polymer films, cast from $CHCl_3$ solutions, by using a JASCO model 300E FTIR spectrometer.

Molecular weights ($M_n$, $M_w$) and molecular weight distributions (MWDs) were measured with a Knauer gel permeation chromatography using ChromGate software Version 2.5, Knauer WellChrom Interface Box V7566, Knauer RI Detector K-2301, Knauer WellChrom HPLC K-501 pump (10 mL/min), Knauer WellChrom injection valves colon oven (5–85°C). $CHCl_3$ was used as an eluent at a flow rate of 1 mL/min. A calibration curve was generated with 10 polystyrene standards: $2.89 \times 10^6$, $9.73 \times 10^5$, $2.33 \times 10^5$, $1.2 \times 10^5$, $9.0 \times 10^4$, $5.2 \times 10^4$, $9.0 \times 10^3$, 5050, 2950, and 104 Da of low dispersity obtained from Polyscience.

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

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

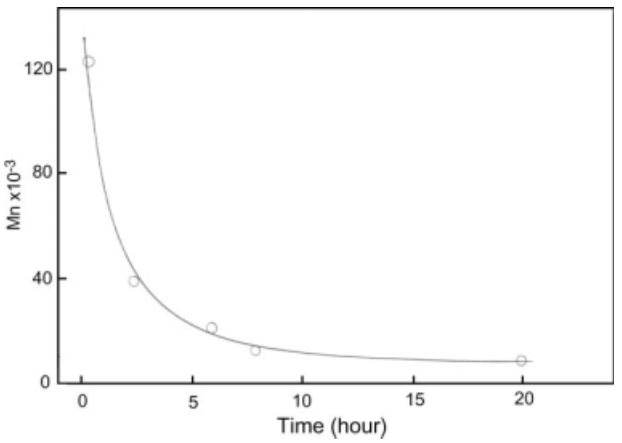



**Figure 1** Variation of the molecular weight of PHBV with the refluxing time.

## RESULTS AND DISCUSSION

Chemical modification of PHA with nondegradable polymers via the synthesis of graft and block copolymers of PHA was also very important to improve the physical and mechanical properties of PHAs.[57–64] Chemical modification needs to obtain new materials for some special applications.

### Degradation of PHBV

PHBV is insoluble in most of the organic solvents, and therefore, reducing the molecular weight (MW) helps PHBV to dissolve in common organic solvents. The boiling temperature of 1,2-dichlorobenzene and the melting temperature of PHBV are nearly equal, so PHBV melts and the crystalline structure is disrupted at that temperature. After this process, the MW of PHBV was decreased depending on the refluxing period because of the thermal instability of high-molecular weight PHB.[65–67] Increase in the period of refluxing causes the dramatic decrease in MW of PHBV. MW variation of the PHBV in boiling 1,2-dichlorobenzene at 175°C is shown in Figure 1. When refluxing time varies from 20 min to 20 h, $M_n$ changes from $122 \times 10^3$ to $8.5 \times 10^3$ with the MWD in range between 1.8 and 1.3. Because only linear PS standards were used, the GPC MWs are not accurate and there might be some differences to the true values. However, the GPC measurement was useful to compare the MWs of the PHAs before and after the reaction.

Because PHBHx is already soluble in the mixture of the chlorinated solvents, $CHCl_3/CCl_4$, it was not necessary to degrade PHBHx. Therefore, the chlorination process was applied as received without any degradation process.

**TABLE I**
**Results and Conditions of the Chlorination Reactions of the PHBHx ($M_n$ = 800,000; MWD = 1.3) and PHBV-7 ($M_n = 12.2 \times 10^{-4}$ Da)**

| Run no. | PHA-Cl, g | Chlorination time, h | Yield, g | Cl- wt.% | $M_n$ ($\times 10^{-3}$) | MWD |
|---|---|---|---|---|---|---|
| PHBHxCl-1 | 4.0 | 3.0 | 4.7 | 25 | 35 | 2.0 |
| PHBHxCl-4 | 3.5 | 3.0 | 5.2 | 43 | 24 | 2.2 |
| PHBHxCl-5 | 3.5 | 3.0 | 4.7 | 28 | 43 | 2.1 |
| PHBHxCl-9 | 3.5 | 3.0 | 3.6 | | 3.9 | 1.7 |
| PHBHxCl-10 | 3.5 | 4.0 | 3.9 | 21 | 9.5 | 1.7 |
| PHBHxCl-11 | 3.5 | 5.0 | 4.1 | 22 | 17 | 1.9 |
| PHBHxCl-12 | 3.5 | 5.5 | 3.8 | 27 | 21 | 1.9 |
| PHBHxCl-13 | 3.5 | 3.5 | 4.8 | 22 | 23 | 1.9 |
| PHBVCl-7-3 | 3.0 | 2.5 | 3.4 | 10 | 38 | 1.9 |
| PHBVCl-7-4 | 3.0 | 4.5 | 3.7 | 30 | 26 | 1.7 |
| PHBVCl-7-5 | 3.0 | 5.0 | 3.6 | 34 | 20 | 1.8 |

### Synthesis of PHBV-Cl and PHBHx-Cl

Chlorination reactions were carried out in PHBV and PHBHx solutions in a $CHCl_3/CCl_4$ mixture with $Cl_2$ gas. Results and conditions of some of chlorination reactions are listed in Table I. When chlorine gas introduced to the PHA solutions in different times from 2.5 to 5.5 h, chlorine in the chlorinated samples varied from 10 to 43 and $M_n$ varied from $3.9 \times 10^3$ to $43 \times 10^3$. Most of the chlorinated samples were white semielastomeric solids, but some samples were waxy and viscous liquid at room temperature. Substitution reactions of the chlorine atom occurred mainly on H-atoms in the saturated hydrocarbon side chains. Hydrogen chloride formation during chlorination reaction has led to the PHA hydrolysis. Therefore, decrease in MWs of the polymers was observed. It was observed that decreases in the MWs of chlorinated PHBV were increased with the increase in the chlorine content in PHBV, which is depending on chlorination reaction time (compare Run No.7-3, 7-4, and 7-5 for PHBVCl in Table I). However, in case of PHBHx, the results could not be generalized. PHBHx is soft-sticky, elastoplastic because of the plastify effect of hexanoate units and has high solubility in chlorine solvents, whereas PHBV is brittle and has low solubility in chlorine solvents. Therefore, PHBHx was used directly as original with high MW without doing any degradation process, which is applied in the case of PHBV to improve its solubility. Because of that PHBHx might be exhibited different chlorination phenomena.

The fractional precipitation is a useful tool both to purify block copolymers and also to determine $\gamma$ value, which is a volume of nonsolvent ($CH_3OH$), mL/volume of solvent ($CHCl_3$), mL. The oligomers were separated from high MW ones. $\gamma$ Values for PHBVCl-7 were changing in range between 0.3 and 1.1, whereas that of unchlorinated-PHBV-7 was 2.0–2.2. Similarly, $\gamma$ values for the chlorinated-PHBHx samples were changing in range between 0.2 and 1.0, whereas that of unchlorinated PHBHx was 2.8–3.0. This shift to lower values in $\gamma$ comes from the good solubility of the PHA-Cl in chloroform, as expected. The other reason is that the lower MW of the higher $\gamma$ value. For example, $\gamma$ value for PHBHx-Cl-5 with $M_n$ 43,000 is 0.2–0.3, whereas $\gamma$ value for PHHx-Cl-9 with $M_n$ 3900 is 0.8–1.0.

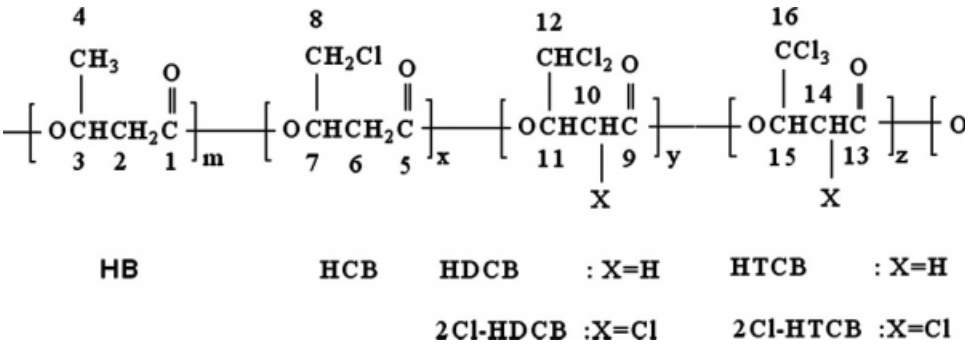
Structural analysis of the chlorinated samples was carried out using $^1$H-NMR techniques. Hydrogen assignments of the PHBHx-Cl for the $^1$H-NMR spectra are shown in Scheme 1.

For samples with high-chlorine contents, in addition to 3HB and 3-hydroxy-chloro-butyrate, HCB, repeating units, 4,4-dichloro-3-hydroxybutyrate (HDCB), 4,4,4-trichloro-3-hydroxybutyrate (HTCB), 2-4-4-trichloro-3-hydroxybutyrate (2Cl-HDCB), and 2,2,4,4-tetrachloro-3-hydroxybutyrate (2Cl-HTCB) units could also be observed by $^1$H-NMR spectroscopy. All chlorinated PHBHx and PHBV samples indicated the characteristic signals of the chlorinated groups together with the unchlorinated PHB units (Fig. 2). When we referred carbon numbers of the chlorinated moieties in Scheme 1, the characteristic assignments in the $^1$H NMR spectrum of the PHBHx_C1 sample can be shown below: $\delta$ (ppm) **2**: 2.89, **3**: 5.30, **4**: 1.39, **6**: 2.97–3.09, **7**: 5.45, **8**:

In FTIR spectra of PHBV and PHBHx, the carbonyl vibration is located around 1730 $cm^{-1}$. On the other hand, PHBV-Cl and PHBHx-Cl have their characteristic C—Cl and carbonyl vibrations at 760 and 1760 $cm^{-1}$, respectively. Intensity of C—Cl peak reflects the increase in the amount of chlorine in the polyester molecule (FTIR spectra are not shown).

Thermogravimetric analysis of the chlorinated samples indicated the decomposition temperatures ($T_d$) 222–230°C for PHBV-Cls and 230–273°C for PHBHx-Cls.

Chlorination of PHBV disrupts the crystallinity of the polymer, as well as the nature of molecular interactions, leading to the changes in $T_g$ and $T_m$




**Scheme 1** Hydrogen assignments of the PHBHx-Cl for the $^1$H-NMR spectra.

values. The thermal behavior of PHBV-Cls was determined by DSC. Although unchlorinated-bacterial PHBV has $T_g$ value of −1°C and $T_m$ value 145°C, PHBV-Cl samples have $T_g$ at 33 and $T_m$s at 53 and 123°C.

Presumably, steric effect of the chloride might have increased the $T_g$ of PHBV-Cl.

### Synthesis of PHA-*g*-PTHF graft copolymers with $AgSbF_6$+PHA-Cl catalyst system

We have recently reported the brush-type block/graft copolymer synthesis starting from PHA-Cl via atom transfer radical polymerization.[68,69] In this work, we used the chlorides with silver salt to initiate cationic polymerization of tetrahydrofurane. PHA-*g*-PTHF graft copolymers were synthesized employing bulk or solution polymerization methods in the presence of chlorinated-PHAs and $AgSbF_6$. The reaction conditions and results are shown in Table II for bulk and for solution polymerization. The solution polymerization was carried out after a thorough solubility tests for $AgSbF_6$ in a series of solvents. Acetonitrile and pyridine were found to be good solvent for cationic polymerization, whereas dichloromethane, benzene, ethylacetate, toluene, and acetone were poor solvents. Trichloromethane reacted with $AgSbF_6$ violently. However, acetonitrile was used as a solvent for the cationic polymerization experiments.

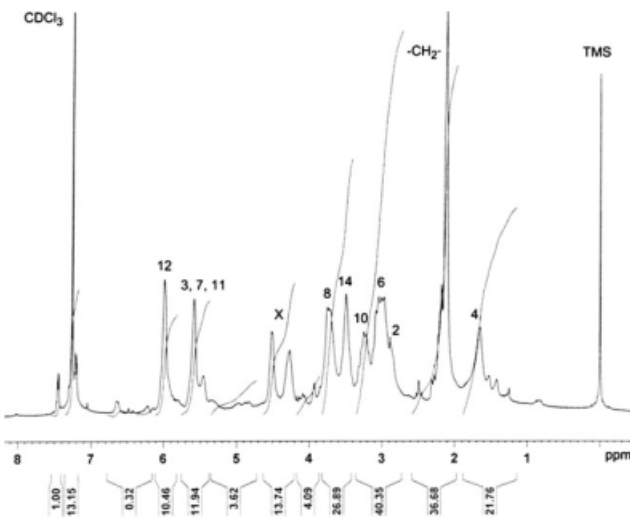



**Figure 2** $^1$H-NMR spectrum of the PHBHx-Cl-1.

Scheme 2 indicates that chlorides of PHA-Cl react with $AgSbF_6$ resulting in the precipitation of AgCl and formation of carbocation on polyesters where $SbF_6^-$ is the counterion. These carbocations initiate the polymerization of THF to form PHA-*g*-PTHF graft copolymers.[47–50] After the reaction was completed, polymer solution separated from AgCl(s) by decantation was precipitated in water/methanol mixture.

Cationic polymerization of THF in the bulk was more productive than cationic polymerization in the solution, because of the dilution effect of solvent (compare Run No. B-7-5 with B-7-5s in the Table II). Furthermore, it is observed that decreases in the MWs of copolymers because of hydrolyses of PHA backbone during cationic polymerization due to $AgSbF_6$ salts are similar in these two experiments.

Increasing the amount of $AgSbF_6$ simultaneously with extension of polymerization time also increased the extent of hydrolysis of PHA backbone during THF polymerization, not only in the presence of solvents but also in the absence of solvents.

MWs were determined by GPC. This result revealed that PHA-*g*-PTHF graft copolymers had lower MWs than that of the starting sclPHA-Cl, which can be explained by taking into account of hydrolysis of PHA blocks by $AgSbF_6$. Literature data support this explanation.[70–76] After cationic polymerization, the graft copolymers obtained had still chloride at around 10–12 wt %, which we can conclude that partial chloride has been introduced in the production of cationic species. $^1$H-NMR spectra of PHA-*g*-PTHF copolymers were containing characteristic signals arising from PHA and PTHF blocks: δ

**TABLE II**
**Results and Conditions of the Cationic Bulk and Solution (Solvent: Acetonitrile, AcN) Polymerization of THF Initiated by $AgSbF_6$ and PHA-Cl System**

| Run no. | $[Ag^+]$ (mM) | PHA-Cl Type | PHA-Cl Amount (g) | THF (mL) | AcN (mL) | Polm. temp (°C) | Polm. time (h) | Yield (g) | $M_n$ ($\times 10^{-3}$) | MWD |
|---|---|---|---|---|---|---|---|---|---|---|
| Bulk Polym. | | | | | | | | | | |
| B-12-3 | 25 | PHBHxCl-4 | 2.0 | 10 | – | 30 | 29 | 2.3 | 22 | 1.3 |
| B-7-5 | 360 | PHBV7Cl-5 | 1.0 | 5.0 | – | 40 | 31 | 2.0 | 2.6 | 1.5 |
| B-7-10 | 380 | PHBV7Cl-10 | 1.0 | 3.0 | – | 40 | 23 | 2.3 | 3.8 | 1.9 |
| B-12-12 | 390 | PHBHxCl-10 | 1.0 | 5.0 | – | 40 | 24 | 3.1 | 7.9 | 1.6 |
| Solution Polym. | | | | | | | | | | |
| B-12-8 | 48 | PHBHxCl-12 | 2.6 | 20 | 10 | 30 | 26 | 2.6 | 8.8 | 1.9 |
| B-12-9 | 73 | PHBHxCl-12 | 2.5 | 10 | 10 | 30 | 26 | 2.2 | 13 | 1.6 |
| B-12-6 | 91 | PHBHxCl-4 | 1.0 | 2 | 5 | 30 | 96 | 0.8 | 6.0 | 1.3 |
| B-12-10 | 194 | PHBHxCl-13 | 5.0 | 10 | 5 | 30 | 44 | 5.2 | 4.3 | 1.6 |
| B-12-7 | 262 | PHBHxCl-1 | 1.0 | 2 | 2 | 30 | 96 | 0.7 | 3.9 | 1.3 |
| B-7-5(s) | 332 | PHBV7Cl-5 | 1.0 | 5 | 2 | 40 | 31 | 1.1 | 2.4 | 1.5 |

(ppm): 1.6 (b,c for PTHF), 3.4 (a,d for PTHF); 2.1 (—$CH_2$—side groups of PHBHx), and 3.7(8), 5.6(11), and 6.0(12) for PHA-Cl blocks (please see Scheme 1 for the signals marked of the PHA-Cl groups as 8, 11, 12; and see Scheme 2 for the signals marked of the PTHF groups as a,b,c,d).

Polymer contents of PHA-*g*-PTHF graft copolymers were calculated from the integral area ratios of the PHA signals at 1.42 ppm and of PTHF at 3.42 ppm. PHA contents were found in range 7 mol % for B-1210, 12 mol % for B-128, and 18 mol % for B-129. PHA contents of PHA-*g*-PTHF synthesized in nonsolvent medium. Here, PHA contents were varying from 5 to 7 mol %. Therefore, solution cationic polymerization is included to be preferred in the synthesis of graft copolymer initiated by PHA-Cl and the silver salt. The PHA is only the minor composition in the final material; however, even small amount of PHA will be enough to cleave long chain macromolecule in to small parts. Therefore, these small PHA blocks in the chains make the graft/block copolymers biodegradable.

FTIR spectra of PHA-*g*-PTHF graft copolymers reveal characteristic peaks for both blocks, which verifies the formation of copolymer structure. Strong and spread-out band at 1150 $cm^{-1}$ for —C—O—C— ether groups of PTHF and a sharp C=O carbonyl peak of PHA at 1760 $cm^{-1}$ and unreacted C—Cl groups at 760 $cm^{-1}$ were observed.

Thermal analysis was carried out using thermogravimetry. Figure 3(a) contains a TGA curve for this graft copolymer. In the thermogram of PHA-*g*-PTHF graft copolymer, the peaks for the PHA and PTHF blocks overlap because these blocks decompose approximately at the same temperature range; at 239°C for PHA and at 256.5°C for PTHF block. They can only be differentiated by the splitting at the tip of the peak.

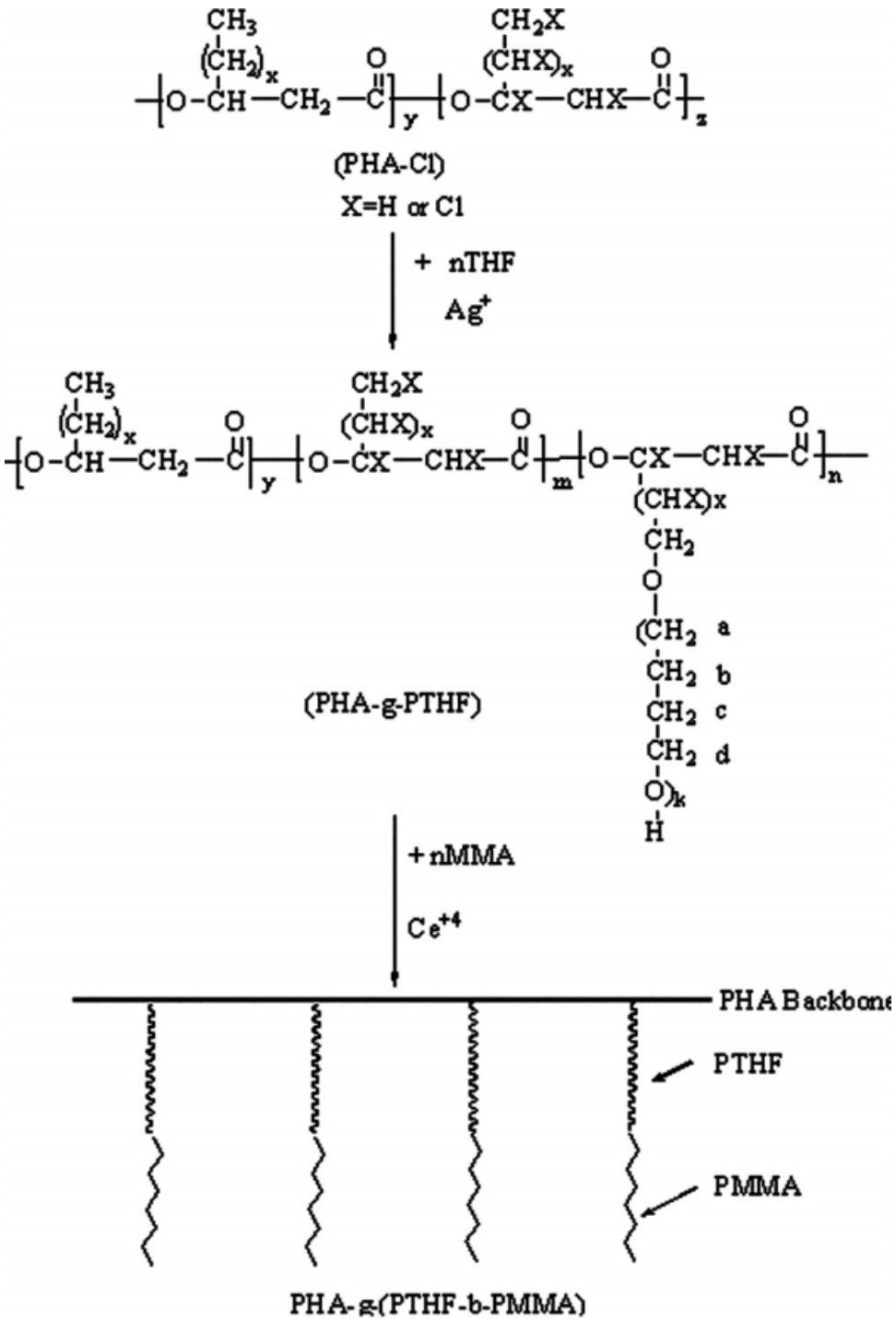
### Synthesis of PHA-*g*-(PTHF-*b*-PMMA) multiblock copolymers

PHA-*g*-(PTHF-*b*-PMMA) multiblock copolymers were synthesized by the free radical redox polymerization of MMA at 45°C initiated with the redox catalyst system of the hydroxyl ends of the PTHF segments in the presence of $Ce^{4+}$. The polymerization mechanism of the PHBV-*g*-(PTHF-*b*-PMMA) multiblock copolymerization synthesis is given in Scheme 2. The optimum concentration values for the initiators cerium ammonium nitrate (CAN) and nitric acid ($HNO_3$) for the redox polymerization reported recently.[56]

The initiator CAN was prepared as 0.05 mol/L in 0.5 mol/L $HNO_3$ and 3.0 mL of the solution was used for all polymerization reactions.[50] To increase the water solubility of monomer (methyl methacrylate) and diols (PHA-*g*-PTHF graft copolymers), surface active agent tetrabutylammonium hydrogen sulfate (TBAHS) was used. It was observed that yield was proportional to the amount of starting -diol. Polymerization conditions and results are collected in Table III.

The experimental data for MB-12-11(4) and MB-12-11(2) clearly show the correlation that an increase in monomer concentration (methyl methacrylate) increases the polymer yield as well as MW while it causes a decrease in $\gamma$ value. Duration of polymerization also directly affects polymer yield and MW in positive manner. We can design the block/graft copolymer structure as shown in Scheme 2: PTHF blocks cover the PHBV blocks in the center, the PMMA blocks are the outer shells that covered the PTHF-PHBV blocks. Thus, brush-multiblock copolymers occur.

The $^1$H-NMR spectra of the multiblock copolymers were also containing characteristic signals of the




**Scheme 2** Reaction design of the synthesis of (PHA-*g*-PTHF)-*b*-PMMA multiblock copolymers.

every block as shown in Figure 4: δ (ppm): PTHF segment: 1.61 for b, c (—$CH_2$—) and 3.41 for a, d (—$CH_2O$—). PHBHx-Cl segments: 1.43 for (—$CH_3$), 2.03 for (—$CH_2$—), 3.74 for $CH_2Cl$— group of HCB), 5.30 for (—CH—). PMMA segments: 0.84–1.01–1.21 for —$CH_3$, 1.81–1.93 for —$CH_2$—, 3.59 for –$OCH_3$.

Figure 5 shows the FTIR spectrum of PHA-*g*-(PTHF-*b*-PMMA) (MB-12-9-2) multiblock copolymer. In the spectrum, characteristic carbonyl (C=O) peak for both PMMA and PHA groups can be seen clearly at 1730 $cm^{-1}$. Etheric (—C—O—C—) absorption band for PTHF block is at 1150 $cm^{-1}$. Unreacted C—Cl groups are still observed at 760 $cm^{-1}$.

Decomposition temperatures for the synthesized PHA-*g*-(PTHF-*b*-PMMA) multiblock copolymers were also determined using thermogravimetric analysis [Fig. 3(b)]. We have observed that the $T_d$ of the hard PMMA blocks shifted to 400°C from 430°C,

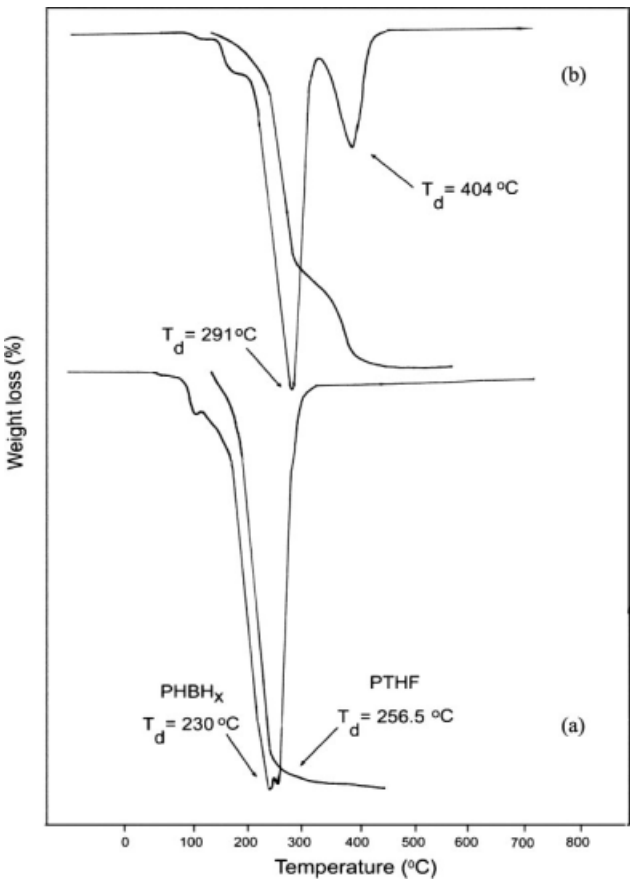



**Figure 3** TGA thermogram of (a) PHA-*g*-PTHF graft copolymer (Sample: B-12-8, in Table II), (b) PHA-*g*-(PTHF-*b*-PMMA) multiblock copolymer (Sample: MB-12-8 (2), in Table III).

and the decomposition temperatures of the other blocks shifted to 290°C from $T_d$ = 260°C for PTHF and from $T_d$ = 230°C for PHA. The peak observed at about 185°C can be attributed to the decomposition

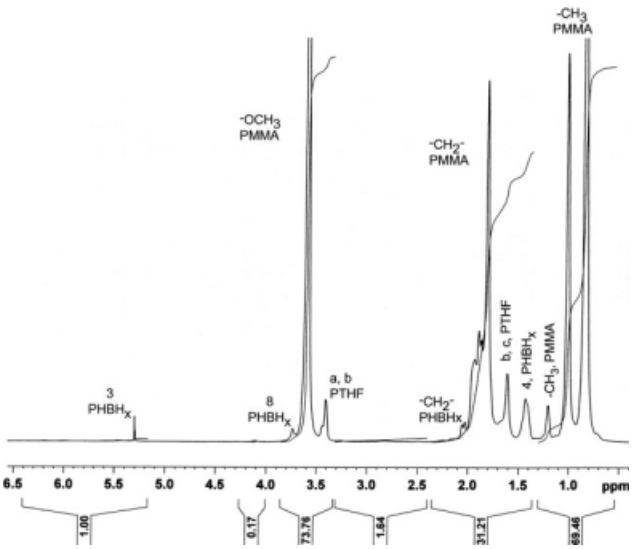



**Figure 4** $^1$H-NMR spectrum of (PHA-*g*-PTHF)-*b*-PMMA multiblock copolymer (Sample: MB-12-11 (3), in Table III).

of the oligomers. The peak areas may reflect directly the contents of PHA-*g*-PTHF copolymers and PMMA. But in this case, ester side bands of the PMMA have overimposed together with the PTHF, PHA blocks. The small shoulder on the sharp peak at around 290°C can be attributed to decomposition of the ester group of PMMA. Taking into account of the peak at 290°C also includes nearly half of the PMMA blocks. DSC traces of some multiblock copolymer samples were also taken. But we have not observed $T_m$ or $T_g$s in DSC traces. Probably, $T_m$s of low MW of THF and PHB segments in the copolymer disappeared. Percentages for PHA-*g*-PTHF graft copolymers had previously been calculated from $^1$H-NMR spectra. These and calculated % PHA-*g*-PTHF from TGA can be used to calculate % PHA and %

**TABLE III**
**Results and Conditions of the Free Radical Polymerization of MMA by ($Ce^{+4}$/-diol Redox System) Initiated by (PHA-*g*-PTHF) Copolymers at 45°C**

| | (PHA-*g*-PTHF) | | | | | Fractional precipitation | | | |
|---|---|---|---|---|---|---|---|---|---|
| Run no. | Type | Amount (g) | MMA (mL) | Polm. time (h) | Yield (g) | γ | (wt %) | $M_n$ ($\times 10^{-5}$) | MWD |
| MB-12-7 | B-12-7 | 0.3 | 2.0 | 2.0 | 1.27 | 2.8–3.3 | 86 | 2.88 | 1.9 |
| MB-12-8 | B-12-8 | 0.3 | 2.0 | 2.0 | 1.50 | 2.0–2.5 | 89 | 2.13 | 1.8 |
| MB-12-9 | B-12-9 | 0.3 | 2.0 | 2.0 | 1.53 | 2.0–3.3 | 88 | 2.21 | 1.6 |
| MB-12-10 | B-12-10 | 0.3 | 2.0 | 2.0 | 1.55 | 2.6–3.3 | 87 | 2.50 | 1.4 |
| MB-12-8(2) | B-12-8 | 1.0 | 2.0 | 1.5 | 2.10 | 2.6–3.2 | 70 | 1.29 | 2.4 |
| MB-12-9(2) | B-12-9 | 1.0 | 2.0 | 1.5 | 1.79 | 2.5–3.0 | 67 | 1.18 | 2.4 |
| MB-12-12 | B-12-12 | 0.3 | 1.0 | 2.0 | 0.85 | 3.3–4.5 | 58 | 1.28 | 2.0 |
| MB-12-12(2) | B-12-12 | 0.3 | 1.0 | 4.0 | 1.00 | 3.3–4.5 | 43 | 1.50 | 2.1 |
| MB-12-11(2) | B-12-11 | 0.3 | 1.0 | 2.0 | 1.20 | 3.9–4.9 | 38 | 0.74 | 1.5 |
| MB-12-11(3) | B-12-11 | 0.3 | 1.0 | 4.0 | 1.22 | 3.8–5.0 | 40 | 0.85 | 1.6 |
| MB-12-11(4) | B-12-11 | 0.3 | 2.0 | 2.0 | 2.00 | 3.3–4.0 | 67 | 0.98 | 2.3 |

0.5 mol/L $HNO_3$ in 0.05 mol/L 3.0 mL [$Ce^{+4}$].
γ = $CH_3OH$(nonsolvent)/$CHCl_3$(solvent), $\gamma_{(PHBV3)}$ = 2.0–2.2, $\gamma_{(PHBHx)}$ = 2.8–3.0, $\gamma_{(PTHF)}$ = 7.0–7.5, $\gamma_{(PMMA)}$ = 2.2–2.7.

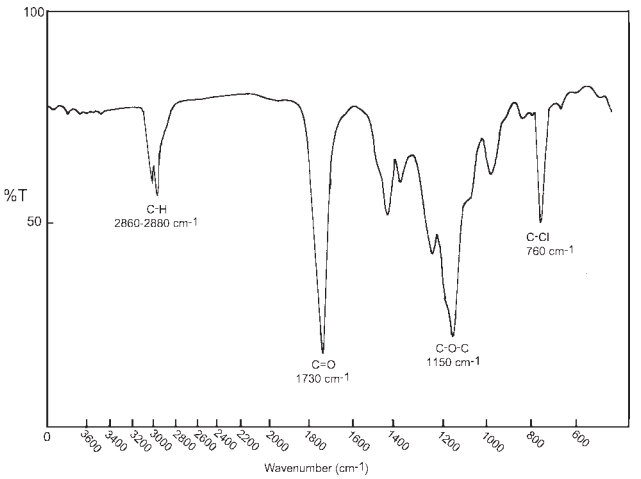



**Figure 5** FTIR spectrum of (PHA-*g*-PTHF)-*b*-PMMA multiblock copolymer (Sample: MB-12-9 (2), in Table III).

PTHF. Copolymer contents of PHA, PTHF, and PMMA segments in the multiblock copolymers were expected in mol % at around 5–15, 20–40, and 56–75, respectively, from the TGA curves and NMR spectra.

## CONCLUSIONS

Chlorinated PHAs for further modification can be successfully used in the synthesis of the multiblock/graft copolymers via transformation polymerization of cationic to free radical routes. Carbocations formed along with the chlorinated polyester chain by the abstract of chlorine atom with $Ag^+$ initiate the cationic polymerization of THF to form brush-type graft copolymers. Hydroxyl ends of PHA-PTHF brushes add MMA monomers in the presence of the Ce(IV) salt leading to PHA–PTHF–PMMA multiblock copolymers. Thus, a new simple method for the diversification of microbial polyesters has been carried out.

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