Functionalization of Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) Films via Surface-Initiated Atom Transfer Radical Polymerization: Comparison with the Conventional Free-Radical Grafting Procedure

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ABSTRACT: We modified hydrophobic poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV) films with hydrophilic chains to control their surface properties. We designed and investigated surface-initiated atom transfer radical polymerization (SI-ATRP) to modify the PHBHV films by grafting poly(2-hydroxyethyl methacrylate) (PHEMA) from the surface. This method consisted of two steps. In the first step, amino functions were formed on the surface by aminolysis; this was followed by the immobilization of an atom transfer radical polymerization initiator, 2-bromoisobutyryl bromide. In the second step, the PHEMA chains were grafted to the substrate by a polymerization process initiated by the surface-bound initiator. The SI-ATRP technique was expected to favor a polymerization process with a controlled manner. The experimental results demonstrate that the grafting density was controlled by the reaction conditions in the first step. The grafted films were analyzed by Fourier transform infrared spectroscopy, contact angle testing, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The results show that grafted chains under the SI-ATRP method were preferentially located on the surface for surface grafting and in the bulk for conventional free-radical polymerization initiated by benzoyl peroxide. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 184–194, 2011

Key words: biocompatibility; biodegradable; polyesters

INTRODUCTION

In recent years, bioerodible and biodegradable polymers have attracted scientific and technological interest not only as environmentally friendly materials but also for biomedical applications. Among biodegradable polymers, poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV) constitute a class of thermoplastic polyesters obtained from renewable resources, such as glucose and propionic acid, through bacterial activity.[1–4] Some poly(hydroxyalkanoates) (PHAs) exhibit thermal and mechanical properties similar to those of traditional thermoplastics, such as polyethylene and polypropylene. PHAs are promising materials for medical or environmental applications because of their biodegradability and biocompatibility.[5] These polymers could be advantageously used as bacterial adhesion supports for wastewater treatment. The advantages of PHAs include their biodegradability; they should be used as a source of carbon for bacteria, which could lead to the development of processes for recycling water within bacteria without an additional carbon source.[6] For cell attachment to polymer surfaces, a modification of the surface is required to improve the cell adhesion. It is widely known that the adhesion and proliferation of different types of cells on polymeric materials depend on the surface characteristics, such as wettability (hydrophilicity or surface free energy), chemistry, charge, roughness, and rigidity.[7,8]

To trigger the cell–matrix adhesion on PHAs surfaces, several surface-modification techniques have been recently been applied, including alkaline hydrolysis,[9,10] ion implantation,[11] oxygen plasma treatment,[12] γ irradiation,[13] and irradiation with UV light[14] or ozone[15] followed by chemical grafting.[16] Grafting has been considered the most convenient technique for modifying the physical and chemical properties of polymer surfaces because the effects of other treatments, which form polar groups on the surface, are not significant enough. This process sometimes does not last long because polar functional groups formed on the surface tend to overturn readily in the outer surface region and migrate into

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the bulk of the polymer, mainly because of the local motion of polymer segments.[17] Most of them are based on a grafting-from process, where radicals are formed along the polymer backbone, followed by a free-radical polymerization of vinyl monomers.

We previously reported the grafting-from polymerization of 2-hydroxyethyl methacrylate (HEMA) on PHBHV films to modify the hydrophilic balance of PHBHV.[18] HEMA was chosen as a model hydrophilic monomer. Hydrophilic poly(2-hydroxyethyl methacrylate) (PHEMA) exhibited excellent biocompatibility.[19] In that study, the grafting was carried out via a conventional free-radical-initiated process with benzoyl peroxide (BPO) as a free-radical initiator. This process has advantages, including easy and graft yield control. However, because of the presence of free initiator in solution, the polymerization proceeded in an uncontrolled manner, and it was difficult to obtain well-defined graft lengths. A most convenient technique for modifying the surface by the grafting-from technique is to develop a controlled free-radical polymerization to achieve higher control of the composition and a narrow polydispersity of the polymer grafted chains. Atom transfer radical polymerization (ATRP) was first studied by Wang and Matyjasewski[20] and Sawamoto et al.[21] in 1995 and has become widely used because of its ability to create polymers with a low polydispersity and a controlled molar mass. The use of ATRP from a surface allows one to resolve the intrinsic problems of conventional free-radical polymerization and to attach well-defined polymer brushes on various types of substrates.[22] Furthermore, this technique is applicable to a wide range of functional monomers under mild conditions. Surface functionalization with ATRP has mostly been studied with planar inorganic substrates, such as gold or quartz,[23,24] but also with polymers, such as poly(propylene),[25] poly(ethylene terephthalate) (PET),[26] nylon, poly(ε-caprolactone) (PCL),[27] and cellulose.

In this article, we report on the use of surface-initiated atom transfer radical polymerization (SI-ATRP) to tailor the functionality of PHBHV films with covalently tethered polymer brushes. A simple two-step method was developed for the covalent immobilization of an ATRP initiator on the PHBHV film. The polymerization of HEMA was achieved via SI-ATRP. The influence of various parameters, such as the monomer concentration, temperature, and reaction time, on the grafting density was studied and compared with our previous report on the grafting of PHEMA onto PHBHV as initiated by BPO.[18] The location of the grafted chains was investigated for both grafting processes.

EXPERIMENTAL

Materials

The polymer used in this study was PHBHV with 12% 3-hydroxyvalerate. It was purchased from GoodFellow (London, UK). 2-Bromoisobutyryl bromide (BIBB), ethylenediamine (EDA), copper (I) bromide (CuBr), copper (II) bromide ($CuBr_2$), chloroform, ethanol and *N,N, N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich (Ontario, Canada) and were used as received. HEMA (Aldrich) was passed through a ready-to-use inhibitor-removing column (Aldrich).

Preparation of the PHBHV film

The PHBHV was first purified by dissolution in chloroform in reflux for 2 h (20% w/v) and by precipitation in ethanol. We prepared the films by casting a chloroform solution onto a glass plate. The mixture was then poured onto an automatic film applicator (Sheen Instruments, Redhill, UK) and cast at a rate of 50 mm/s. The films were dried overnight and then dried *in vacuo* to remove the residual solvent. Samples were cut into 3.5 × 2.2 cm^2 pieces. Films with an average thickness of 70 μm were obtained.

Free-radical grafting procedure18

All reactions were heterogeneous and involved PHBHV films. In all cases, the PHBHV film was attached with Teflon linkages to a glass slide and placed in a 100-mL, round-bottom flask containing an aqueous HEMA monomer solution purged with nitrogen for 30 min. For all experiments, the total volume was 50 mL. The required concentration of BPO was dissolved in 2 mL of acetone and added to the polymerization vessel. The vessel was placed in an oil bath adjusted to the polymerization temperature (80°C). The reaction was carried out under a nitrogen atmosphere. After the reaction time was complete, we removed the film from the polymerization vessel and then purified it from the unreacted monomer and residual homopolymer (PHEMA) by washing it in 100 mL of boiling ethanol for 3 h. The washing ethanol was changed once to completely remove the homopolymer from the film. The film was finally dried to a constant weight *in vacuo* at 40°C overnight. The efficiency of the extraction method was tested with a physical blend of PHEMA. After treatment with hot ethanol as described previously, free PHEMA was totally removed. For each concentration, four experiments were carried out.

Functionalization and grafting of the ATRP initiator

Surface aminolysis

Many experiments of surface aminolysis were carried out. The films were treated with different concen-trations of aqueous EDA, with a mixture of EDA and potassium hydroxide (KOH), or with solution of EDA diluted in dimethylformamide (DMF). The films were treated at room temperature or 60°C with continuous stirring for various times. After the reaction, the films were removed from the solution and washed with a large amount of water for at least 3 h at room temperature; the water was changed every hour. Then, the films were dried *in vacuo* at 40°C overnight.

Amine titration

The ninhydrin analysis method was used to quantitatively detect the amount of NH_2 ending groups on the aminolyzed PHBHV films. The unmodified PHBHV film was used as a negative control. Films were immersed in 2 mL of an ethanolic solution of ninhydrin (10 g/L, 0.06 mol/L) in a glass tube. The tube was immersed in boiling water for 20 min. After the reaction, 8 mL of a water/ethanol mixture (62.5/37.5) was added to the glass tube to obtain a final solution with water/ethanol (50/50). The absorbance at 570 nm was measured on a UV–visible spectrophotometer (Perkin-Elmer, Waltham, Massachusetts). A calibration curve was obtained with an ethanolamine solution in ethanol.

Immobilization of the ATRP initiator

The aminolyzed films were immersed in 100 mL of anhydrous diethyl ether containing 3.2 mmol of BIBB and 2.4 mmol of distilled pyridine. The mixture was stirred at room temperature overnight to produce Brominated PHBHV (PHBHV-Br) films to obtain a close quantitative conversion because of the high reactivity of the BIBB. The PHBHV films were thoroughly washed in ethanol (for 3 h; the washing solution was changed every hour after the reaction) to remove any potentially adsorbed initiator and to ensure that only the covalently grafted initiator was present. The films were then dried under reduced pressure.

SI-ATRP grafting polymerization

The PHBHV-Br films were transferred into a solution containing solvent, CuBr, $CuBr_2$, and PMDETA. The mixture of catalysts was previously dispersed under ultrasound to assure complete dissolution in water. We deoxygenated the solution by purging argon through the solution for at least 30 min. Another vessel containing the monomer was also deoxygenated by argon for at least 30 min. Then, the monomer was transferred into a rubber-septum vial containing the primary solution via cannula. The solution was stirred at room temperature or at 80°C. The graft yield (G) was calculated as the ratio of the increase in mass of the PHBHV film ($w_f - w_i$) divided by the initial mass of film (w_i) according to the following equation:

$$G\ (\%) = \frac{w_f - w_i}{w_i} \times 100$$

where w_f is the final mass.

Moreover, the surface area increase was obtained by measurement of the length and the width after grafting and was calculated according to the following equation:

$$\text{Area increase}\ (\%) = \frac{S_f - S_i}{S_i} \times 100$$

where S_i and S_f are the initial surface area and the final surface are after grafting, respectively.

A control experiment of SI-ATRP HEMA was carried out with native PHBHV film instead the functionalized PHA film; because there was no HEMA grafting on the native PHBHV under these conditions, we can conclude that the ATRP initiators were actually immobilized on the functionalized PHA film.

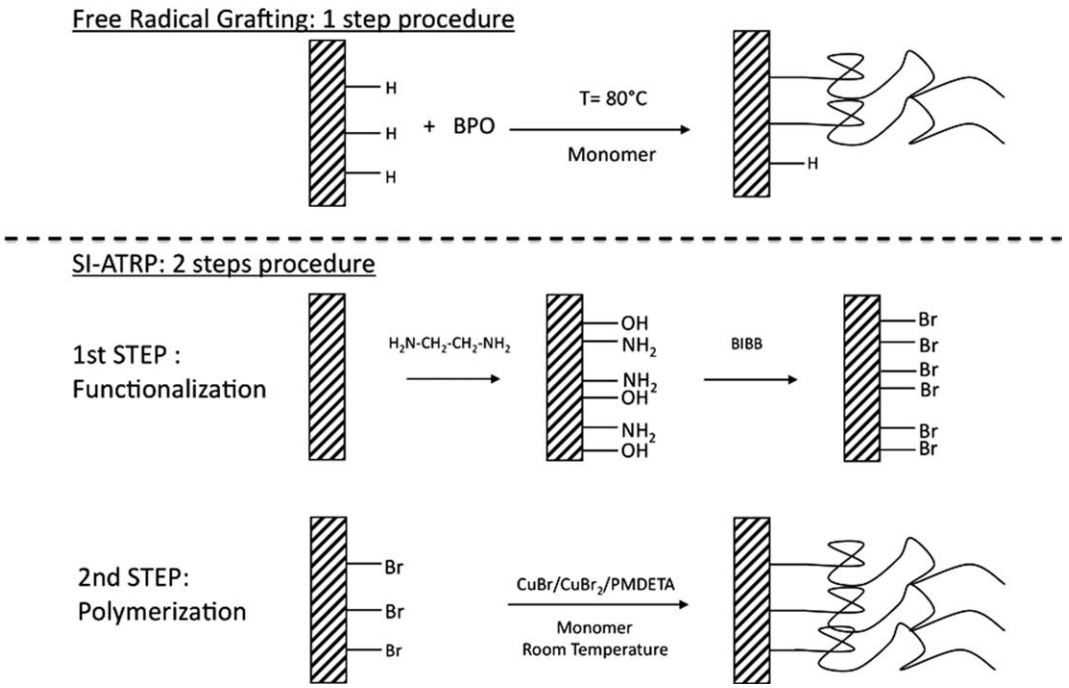
Characterization

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded on a spectrometer (Bruker Tensor 27, Ettlingen, Germany). The spectra of the film surface were obtained with an attenuated total reflection (ATR) instrument with a diamond crystal. The ATR–FTIR spectra were recorded at a resolution of 4 cm^{-1} and an accumulation of 32 scans. The spectra were normalized to the intensity of the carbonyl stretching band at 1720 cm^{-1}.

Measurement of the water contact angle

Static water contact angles of the modified film surfaces were determined by a video-based contact angle apparatus (Digidrop apparatus, GBX instruments, Romans, France). A droplet of deionized water (MilliQ water, 25 μL) was deposited on the surface of a film at room temperature. For each sample, at least five different spots were measured, and the data were averaged.



Scheme 1 Surface modification of PHBHV by SI-ATRP and conventional free-radical polymerization.

Water content measurement

To assess the hydrophilicity of the grafted material, water absorption was carried out by immersion of films into 10 mL of deionized water at 37°C for 24 h. Karl–Fisher titration was performed to quantify the amount of absorbed water. A Metrohm KF 737 coulometer (Herisau, Switzerland) equipped with an Oven Metrohm KF 707 [temperature (T) = 150°C] was used under a nitrogen flow at 200 mL/min. The reactant was Hydranal-Coulomat AG.

Scanning electron microscopy (SEM)

The surface morphologies of the polymer samples, before and after grafting, were observed by SEM. All observations were carried out with a JEOL 6460LV scanning electron microscope (JEOL, Ltd., Tokyo, Japan). The voltage was kept at 15 kV, and the sample was kept at an average distance from the electron gun of about 10 nm. Samples were mounted on aluminum stubs and coated for 120 s at 20 mA with gold with a sputter coater (Edwards Pirani 501, Ltd., Crawley, UK). To observe the films in cross section, samples were incorporated into a low-viscosity methacrylate resin blend (Metafix, Strauer) described previously.[28] They were polished by a series of grindings (silicon carbide grinding paper P320 to P1200) with water as the lubricant. Then, the polishing was performed with progressively finer abrasives with two grades of diamond polishing grit suspensions (9 μm and then 3 μm), followed by alumina (0.05 μm). The polished specimens needed to be sputter-coated with a thin film of conductive material (e.g., carbon).

Energy-dispersive X-ray spectroscopy (EDX)

To assess the localization of the grafted PHEMA onto the PHBHV film, the hydroxyl groups of the PHEMA were esterified with chloroacetyl chloride to observe the element chlorine. The grafted film was immersed in 20 mL of anhydrous diethyl ether containing 2 mL of chloroacetyl chloride and 1 mL of triethylamine. The mixture was stirred for 24 h at room temperature. The reacted film was washed in ethanol for 2 h and dried *in vacuo* at 40°C. Samples were coated with carbon with a sputter coater. The analysis of the elements was carried out by EDX analysis with an OXFORD INCA 300 system (Abingdon, UK). To determine their distribution, Smart Map, Oxford Instruments (Abingdon, UK) acquisition was used. Smart Map performs the simultaneous acquisition of X-ray data from each pixel on the image area. A blank experiment was performed with ungrafted PHBHV and chloroacetyl chloride. The absence of chlorine on the surface of the ungrafted PHBHV showed that the chloroacetyl chloride only reacted in the presence of PHEMA.

RESULTS AND DISCUSSION

The grafting of PHEMA onto the PHBHV film via controlled radical polymerization is outlined in

Scheme 1. This method was compared with the conventional free-radical grafting previously reported.[18] Differences between both processes were the prefunctionalization in the SI-ATRP method and the grafting temperature.

This procedure began with the functionalization of the surface by an aminolysis reaction with diamine. The reaction of the primary amine with the ester group of the PHA backbone led to amide groups with free amine groups and free alcohol groups. These reactive groups were used to immobilize the ATRP initiator (BIBB) onto the PHBHV films. The bromoisobutyryl-functionalized (PHBHV-Br) surface was used in a second step to initiate ATRP of HEMA. PHEMA was polymerized with CuBr/$CuBr_2$/PMDETA as a catalyst system in an aqueous solution. This procedure is usually used to access a brush conformation of macromolecular grafted chains. Details of the surface functionalization process are discussed later.

Functionalization of the PHBHV surface

The surface of the PHBHV films was functionalized by wet chemical aminolysis with EDA. This technique has been widely used to introduce amine functions for biomolecule immobilization onto polymers such as PET,[23,28] PCL,[29] and poly-L-lactide acid (PLLA).[25] Various experimental conditions were tested. Samples treated with high concentrations were brittle; this indicated an important degradation by chain scission, as described in the literature.[29] The fragmentation of the films led us to use milder conditions (1 and 1.5 mol/L). Although there was no difference observed by ATR–FTIR spectroscopy, we observed a drop in the molar masses (results not shown). This result, observed by several authors,[30,31] was the consequence of polymer degradation, which increased with the amine concentration.

Aminolysis was studied under lower concentrations and other conditions (KOH or DMF) to enhance the density of the amino groups without any dramatic degradation of the bulk mechanical properties of PHBHV (Fig. 1). The results show that strong basic conditions (KOH) led to a higher fragmentation of the material. It is known that in DMF solvent, amino functions are more nucleophilic. The treatment in DMF with 1 mol/L diamine at 60°C led to a complete dissolution of the PHBHV film. However, at room temperature, the films were deformed; this indicated the penetration of the solvent into the material. Optimal conditions were achieved with a concentration of 1 mol/L EDA (in water) for 2 h at 60°C.

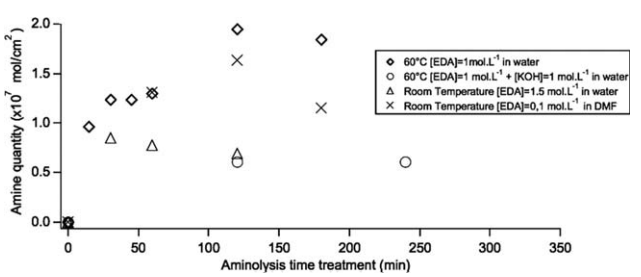


Figure 1 Effect of the aminolysis conditions on the amine quantity.

TABLE I
Influence of the Time of Treatment and EDA Concentration on Aminolysis

PHBHV	Water contact angle (°)	
	Smooth side of the film	Rough side of the film
Ungrafted	87 ± 2	85 ± 1
After immersion in water for 2 h at 60°C	87 ± 1	84 ± 1
After aminolysis (1 mol/L) at 60°C	78 ± 4	68 ± 3
After BIBB treatment	82 ± 2	70 ± 2

The aminolysis was demonstrated by ninhydrin titration. The amine quantity obtained (1.9×10^{-7} mol/cm^2) was in good agreement with results obtained by other authors for the aminolysis of PET[30] and PCL.[31,32] Because of the hydrophobic nature and high crystallinity of PHBHV, we supposed that the aminolysis cleavage was confined to the surface region of the PHBHV, which ensured that the resulting grafting polymer was restricted to the surface.

Immobilization of the ATRP initiator

BIBB was reacted with free amino groups and/or with hydroxyl groups of the PHBHV on the surface film by amidification or esterification to produce the active ATRP initiator on the surface. As previously reported for aminolyzed films, no obvious changes on the ATR–FTIR spectra were observed after the bromoester treatment. The presence of bromide was not detected by ^{1}H-NMR in dimethyl sulfoxide (a common solvent of both PHBHV and PHEMA) at 80°C and EDX. All of these results could be explained by the too-low functional density on the surface of the PHBHV films. We assumed that the wettability of the surface should have changed after chemical treatment. Because the morphology of a material influences the measurement of the contact angle, native PHBHV film was also treated in water during the same time and temperature as used for the aminolysis reaction. Both faces of the films were analyzed because the surface in contact with air during the solvent casting process was rougher than the surface in contact with glass.

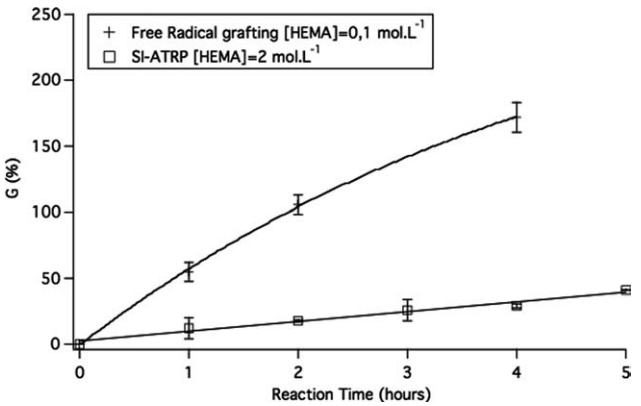


Figure 2 Graft yield as a function of the reaction time.

The results (Table I) show that the aminolysis treatment of PHBHV resulted in a more hydrophilic surface. The water contact angle recorded on the films treated with BIBB was found to increase slightly. This trend correlated with the presence of BIBB groups on the surface. The contact angle of the smooth side was higher than that of the rough side. This trend increased after aminolysis. The values obtained for the control experiment (immersion in water at 60°C) were similar to the contact angles measured for the untreated surface. Thus, the small variation in contact angle was attributed to the functionalization of the surface after BIBB treatment. We supposed that initiator sites were very sparse on the surface.

SI-ATRP of HEMA

SI-ATRP was first conducted by the preparation of a solution of HEMA with CuBr, PMDETA ligand, and $CuBr_2$ in water as solvents at room temperature or 80°C to compare it with our previous study with BPO as a conventional free-radical initiator. The HEMA/CuBr/$CuBr_2$/PMDETA ratio was controlled at 100/1/0.3/1.3, according to previous studies.[19,33] The Cu(I)/Cu(II) ratio of 1/0.3 was selected for its good compromise in the equilibrium between activation and deactivation of the dormant species.[34]

The addition of $CuBr_2$ to the polymerization mixture is usually required to quickly promote equilibrium between the dormant and active chains during Si-ATRP and to limit the polydispersity of the polymer grown on the surface.[19,35,36] Many reports have shown the importance of water in polymerization to accelerate the rate of ATRP of HEMA compared to that conduced in methanol.[35,37,38] The monomer mixture (HEMA in water) did not swell in hydrophobic PHBHV; this ensured that the polymer chains propagated from the initiator sites on the PHA film surface. During polymerization, no precipitation was observed; this indicated that no homopolymerization occurred, as was expected for the SI-ATRP technique.[39]

The kinetic reaction at room temperature was followed by a progressive mass increase of the films. A relative linear plot of the graft yield versus reaction time was obtained; this implied first-order kinetics of the SI-ATRP process (Fig. 2). The linear increase in the graft yield versus the reaction time suggested that the chain was grown from the PHBHV-Br film with a well-defined process.[19] This feature was also in agreement with ideal ATRP kinetics mediated with copper,[40] which was consistent with the accelerating effect of water on the SI-ATRP of HEMA.[41] When compared to the conventional free-radical grafting procedure, the graft yields were higher than those obtained with ATRP, with a lower monomer concentration. This could be explained by the fact that BPO was a very fast and widespread grafting path. However, the difference between both procedures was the reaction temperature, which dramatically affected the grafting process, as expected. To prove this assumption, SI-ATRP was achieved at 80°C, the graft amount increased highly up to 200–300%, and the control of ATRP grafting was more delicate. The increase in the mobility of the macromolecular chains (glass-

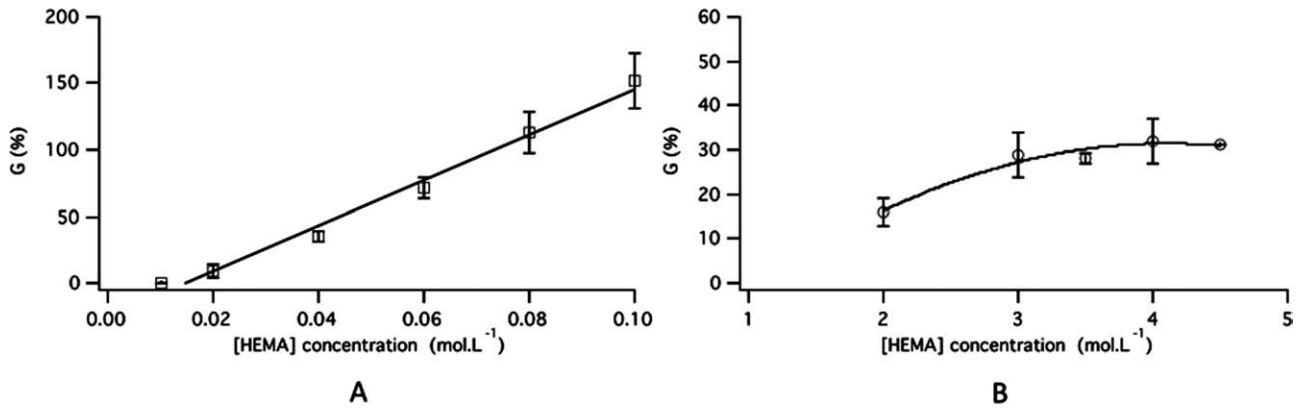


Figure 3 Graft yield as a function of the monomer concentration (reaction time = 2 h at room temperature): (A) SI-ATRP and (B) free-radical polymerization.

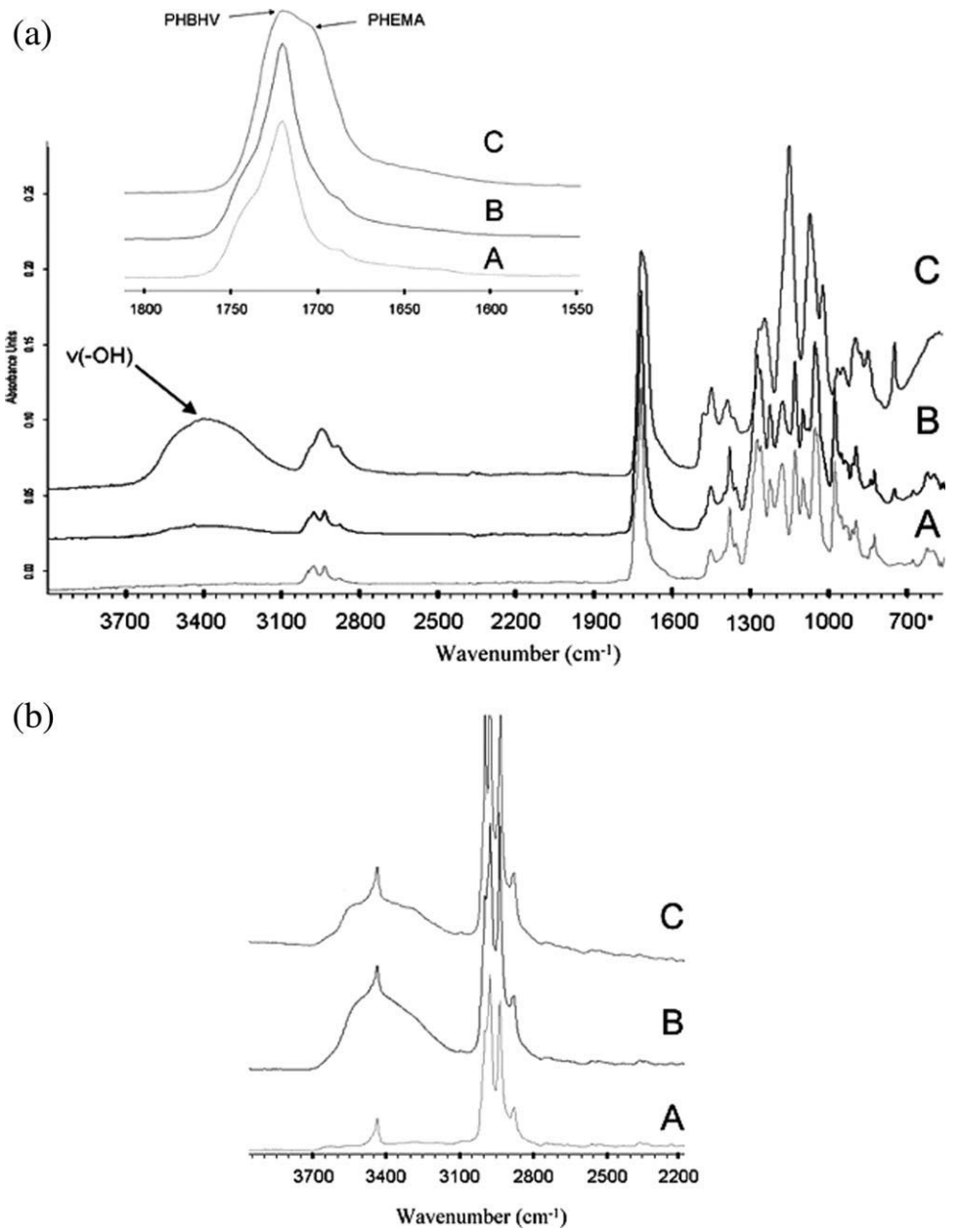


Figure 4 (a) FTIR–ATR spectra of (A) native PHBHV, (B) PHBHV-*g*-PHEMA initiated by BPO ($G = 12\%$), and (C) PHBHV-*g*-PHEMA as observed by SI-ATRP ($G = 10\%$). (b) FTIR spectra in standard transmission enlargement between 2200 and 3800 cm^{-1}: (A) native PHBHV, (B) PHBHV-*g*-PHEMA initiated by BPO ($G = 12\%$), and (C) PHBHV-*g*-PHEMA as observed by SI-ATRP ($G = 10\%$).

transition temperature of PHBHV = 0°C) caused more effective self-diffusion of the monomer and grafted polymer chains into the bulk of the PHBHV film. This assumption was supported by the increase in the surface films. The grafted chains were distributed both within and on the surface of the film, as was observed in the case of the grafting of HEMA initiated by BPO.[18] In the case of BPO, the surface increased when the graft yield was over 100%.

Figure 3 shows the effect of HEMA concentration on the graft yield at a constant time (2 h). The results obtained with BPO indicate that the grafting degree increased highly with the HEMA concentration [Fig. 3(A)]. For Si-ATRP, no result could be calculated with a monomer concentration of 1 mol/L because of the high viscosity of the solution due to the insolubility of PHEMA in water, which entrapped some copper [Fig. 3(B)]. Some catalysts were entrapped inside the gel; consequently, the catalyst mixture, $CuBr/CuBr_2$/ligand, was not constant, and the polymerization was not controlled. In addition, it was impossible to remove the entrapped copper.

At higher than 1 mol/L, a positive effect of increasing HEMA was the solubility of PHEMA in the

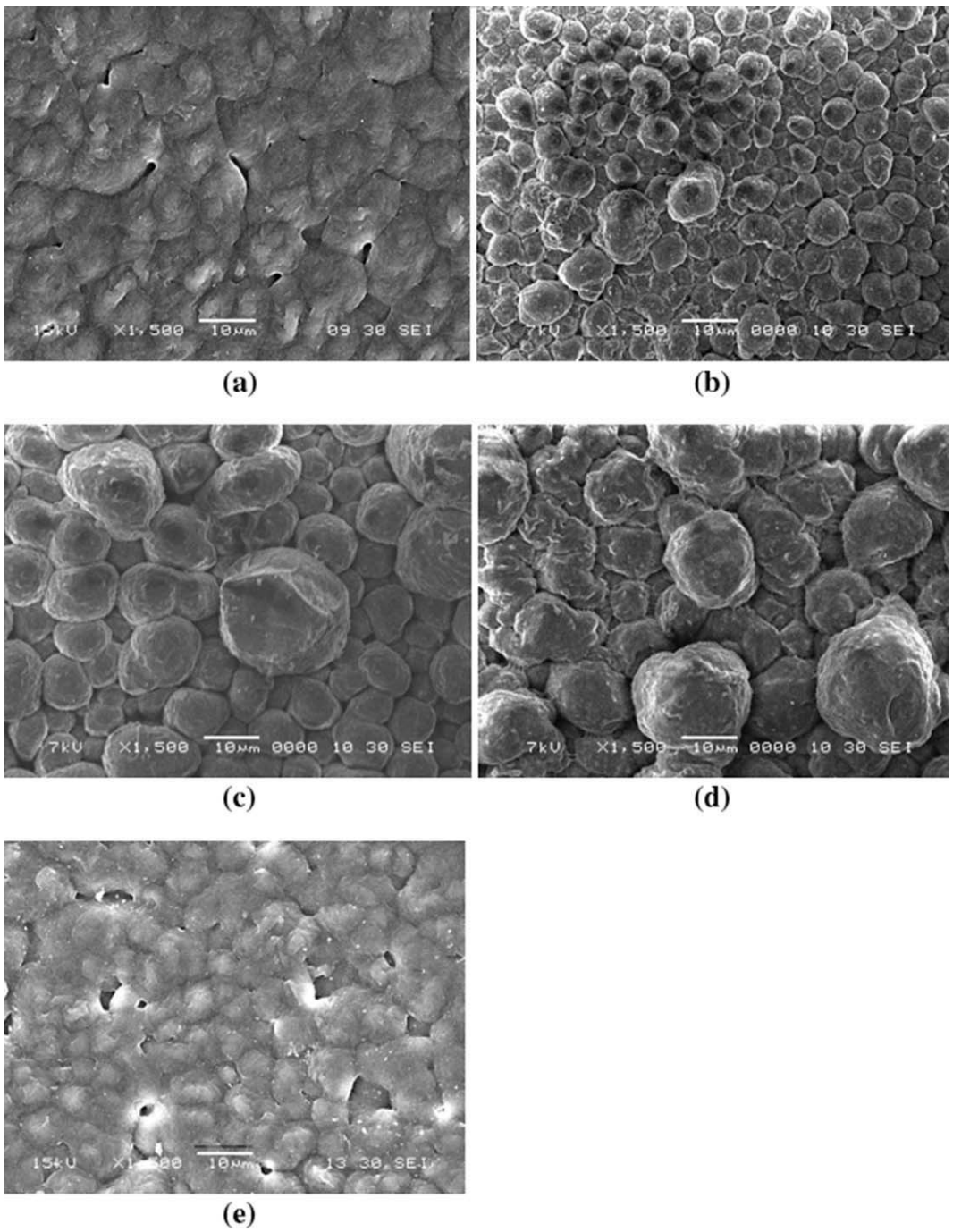


Figure 5 SEM observations of the (a) ungrafted PHBHV, (b) SI-ATRP ($G = 10\%$), (c) SI-ATRP ($G = 16\%$), (d) SI-ATRP ($G = 39\%$), and (e) free-radical grafting ($G = 40\%$).

monomer solution. As shown, the graft yield increased with monomer concentration from a monomer concentration of 2 to 3 mol/L, and then, the graft yield slowed down when the concentration exceeded 3 mol/L.

The slight decrease in the slope at higher monomer concentrations ($>3M$) may have been due to some side reactions as termination. This result was similar to these obtained for the grafting of HEMA on the surface of PET[23] with the presence of water as a polymerization solvent, which is well known to induce a slight amount of transfer reaction.[34]

Characterization

The resulting grafted films were characterized by ATR–FTIR spectroscopy, contact angle measurements, SEM, and EDX. The occurrence of grafting was illustrated by ATR–FTIR analysis. Figure 4(a) shows the ATR–FTIR spectra of the grafted films via SI-ATRP

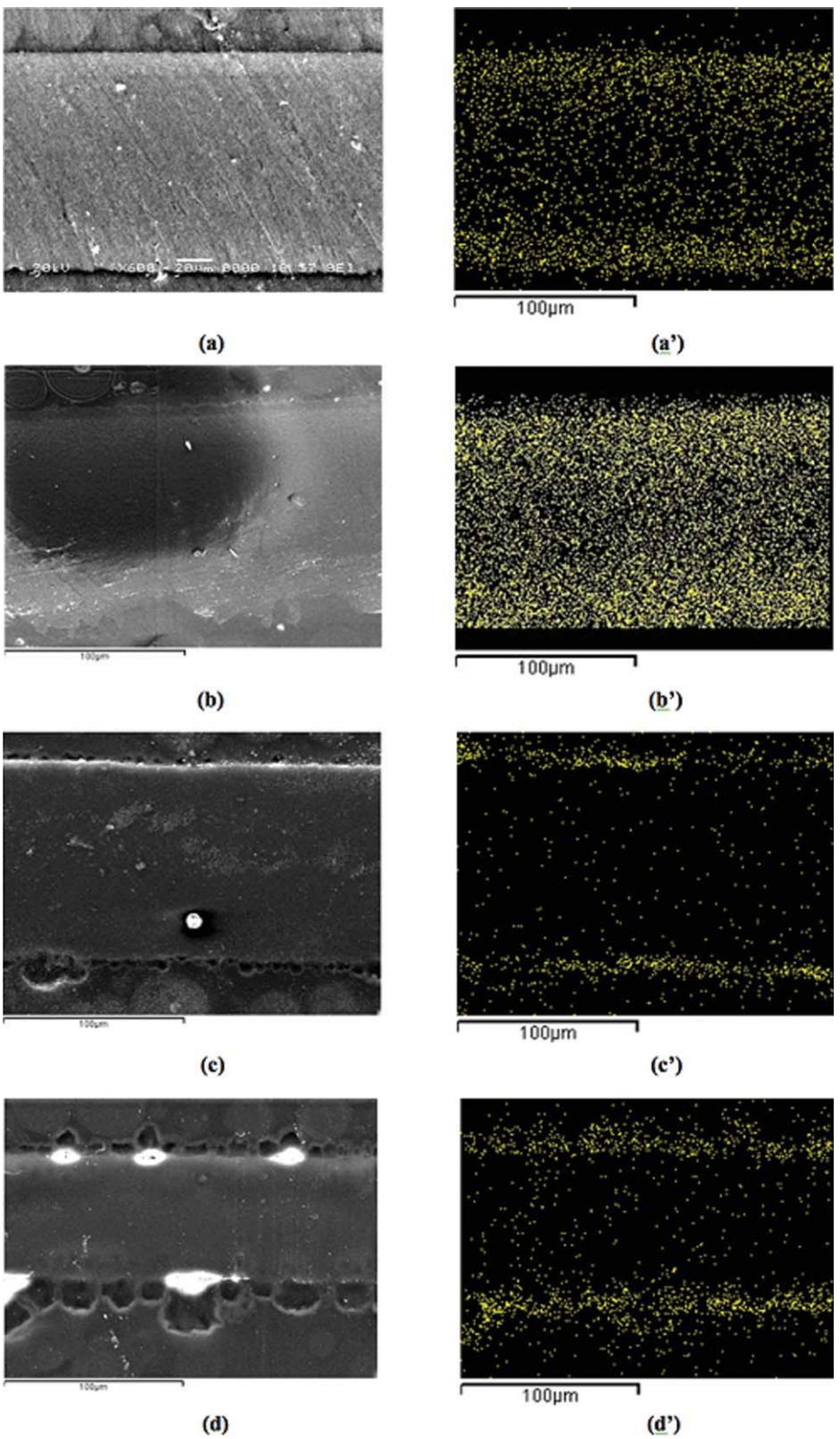


Figure 6 Cross section SEM and EDX analysis of the PHBHV graft initiated by BPO [(a,a′) $G = 15\%$ and (b,b′) $G = 40\%$] and PHBHV grafted by SI-ATRP [(c,c′) $G = 10\%$ and (d,d′) $G = 39\%$]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Water Contact Angles of the Grafted PHBHV

	Water contact angle (°)	
G (%)	SI-ATRP	Free-radical process (BPO)
0	77 ± 3	77 ± 3
10		74 ± 4
17	126 ± 2	
25	105 ± 3	
30		64 ± 5
41	106 ± 5	
70		55 ± 5

(G = 10%) and conventional free-radical grafting (G = 12%). With similar graft yields, the films showed different profiles. The peak corresponding to the —OH from the grafted PHEMA via SI-ATRP was clearly observed. However, in free-radical conditions, the spectra revealed a small hydroxyl peak [Fig. 4(b)]. With regard to carbonyl stretching, the grafted film via SI-ATRP became much broader compared with pure PHBHV and showed the carbonyls of the PHEMA and the PHBHV one, whereas the widening of the carbonyl peak was not visible for free-radical grafting. When the FTIR analyses were performed in standard transmission, similar spectra were obtained [Fig. 4(b)]. The ν(—OH) vibration was clearly present on both modified films. Moreover, this result was in good agreement with the close values of graft yield. ATR–FTIR and standard FTIR suggested that under a conventional free-radical grafting process, the polymerization of HEMA occurred in the bulk, and in the SI-ATRP process, the grafting was principally located on the surface.

Morphological changes of the film surfaces were investigated by SEM. For this purpose, SEM pictures of the film surfaces with different graft yields were studied. As shown in Figure 5(a), the native PHBHV film showed a relatively low porosity. Figure 5(b–d) shows the surface of the ATRP grafted films with graft yields of 10, 16, and 39%, respectively. When compared with conventional free-radical grafted films [Fig. 5(e)], where no change of the surface was observed for graft yields lower than 100% (G = 14%), in SI-ATRP, the surface of the grafted films changed notably from a graft yield of 10%. Figure 5(b–d) illustrates that the film surfaces were covered by grafted PHEMA chains. The surfaces became very rough because of the formation of PHEMA granules. The surfaces were homogeneously covered by grafted PHEMA granules, and the size of the granules increased with the graft yield. This roughness may have resulted from precipitation of PHEMA chains during the desiccation process.

Figure 6 shows the cross-sectional morphologies of the grafted films through inclusion of films in low-viscosity methacrylate resins. The SEM cross-section details of the grafted films via conventional free-radical polymerization showed a smooth homogeneous texture on the surface and in depth. To asses the location of the grafted polymer, EDX was performed on the grafted film. The grafted polymers were tagged with chloroacetyl chloride to introduce chloride groups, which could be detected by EDX. The cross-sectional EDX map showed the presence of chloride groups everywhere on the surface and also in the bulk of the film, which indicated the localization of PHEMA. The density of chloride correlated with the graft yield. The films obtained by ATRP differed from the other one initiated by BPO. They clearly showed that the surface was wavy with the presence of granules; this was attributed to the presence of PHEMA chains on the surface. The thickness of this granular layer increased with the graft yield. The cross-sectional EDX map of the PHBHV-*g*-PHEMA grafted by SI-ATRP showed presence of the chloride, especially on the surface. These results implied that the grafting by SI-ATRP was located only on the surface in comparison with conventional free-radical process, where it occurred on the surface of the film as well but also in the bulk of the film. The roughness and wavy features of the film surfaces obtained by ATRP may have been due to the low amount of initiator sites on the surface. Indeed, it would be very difficult to achieve a high surface coverage with a sparse initiator.

Films obtained by free-radical polymerization were globally smoother than those obtained by ATRP and contained PHEMA on the surfaces. These results agreed with the water contact angles listed and the water adsorption values presented.

A simple and sensitive method for accessing changes of the wetting characteristics of surfaces consists of measuring the water contact angles. Table II shows the variation of the water contact angle as a

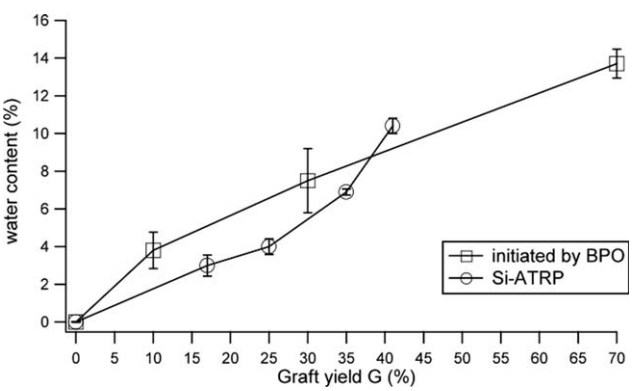


Figure 7 Water content as measured by Karl–Fisher titration after immersion in water at 37°C for 24 h.

function of the graft yield. For the films obtained by the free-radical process, a decrease in the contact angle was correlated with an increase in the graft yield. This was ascribed to the contribution of hydroxyl groups in the PHEMA moieties. In contrast, the contact angles of the grafted films obtained by ATRP were higher than the native ones (ca. 100–120°) and seemed not to have a relation with graft yield. This was caused by the relatively high surface porosity or roughness, as illustrated previously by SEM investigation. To further demonstrate the change of the hydrophilicity balance, grafted films were put in water, and the hydration of the grafted films was quantified. Figure 7 indicates an increase in the water absorption with increasing graft yield; this was in good agreement with the increase in the hydrophilic surfaces' properties. For both polymerization processes, the final polymer surfaces had similar hydrophilicities.

CONCLUSIONS

The chemical grafting of PHBHV films by PHEMA was successfully achieved by the grafting-from technique with an active ATRP initiator on the film surface (PHBHV-Br) and $CuBr/CuBr_2$/PMDETA as the catalyst system in water at room temperature. Several parameters were found to have a great impact on these characteristics, namely, the reaction time and the concentration of the monomer.

The HEMA grafting by the SI-ATRP method was compared to the free-radical grafting initiated by BPO. The results show that the conventional free-radical grafting was not restricted to the surface but occurred also in the bulk, whereas the SI-ATRP showed a larger amount of grafted chains on the surface. SI-ATRP allowed for the selective modification of the polymer surface, which preserved the chemical and/or physical integrity of the bulk polymer, in particular, the biodegradability of the grafted films.

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