# Synthesis and Surface Properties of Fluorocarbon End-Capped Biodegradable Polyesters

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ABSTRACT: We report the synthesis and characterization of a new class of materials based on combining hydrolytically degradable polyesters and fluorocarbon surface chemistry. These materials have surface properties which overcome some of the limitations of polymeric materials in controlled cellular or tissue adhesion properties. Fluorocarbon chains of two lengths ($CF_3(CF_2)_m(CH_2)n$, where F7C1 and F10C2 represent $m = 6$ and $n = 1$ and $m = 9$ and $n = 2$, respectively) have been synthesized as the terminal end groups to L- and DL-polylactides (PLA) and poly(lactide-*co*-glycolide) copolymers. Using both ring-opening polymerization and the substitution of the fluorocarbon at terminal hydroxyl groups, polyesters with 1, 2, and 4 fluorocarbon end groups were obtained (F-polyesters). Angular dependent X-ray photoelectron spectroscopy (XPS or ESCA) revealed that end groups are segregated at the surface. Further, the results show their the surface coverage of fluorocarbon groups increases with increasing the concentration and the length of fluorocarbon end groups. The surface composition of F-polyesters can be controlled by blending these polymers with polyesters or by changing the architecture of fluorocarbon end groups. From ESCA data of F-polyesters after in-vitro hydrolysis at pH = 11.4, results from the F-polyester with a longer fluorocarbon end group (F10C2-) show that the surface erosion occurs at the topmost surface region during the initial hydrolysis period. The F-polyester having a short fluorocarbon group (F7C1-) shows a progressive decrease of surface fluorocarbon concentration as a function of hydrolysis time. This result is explained by a longer retardation time for water permeation into the sample bulk of F10C2-L-PLA due to greater segregation of fluorocarbon groups at the topmost surface.

## Introduction

The surface layer properties of polymers have recently received great attention in practical applications, such as biomaterials, adhesives, paints, coatings, and so on, since these are strongly related to the associated functional properties.[1−13] A desired polymer surface often cannot be obtained from the material itself but through chemical or physical modification. It has been well-known that the component of a lower surface free energy in multicomponent polymeric systems, graft and block copolymers, is preferentially concentrated at the air surface region in order to minimize the air/material interfacial free energy.[4,5,9,11,14] The most common surface modification techniques include blending,[4,14] copolymerization,[5,7,12] chemical surface reactions,[3] flame treatment,[2] and plasma treatment.[1,6,8]

Although blending is an attractive method to change surface properties because of the common use of commercially available polymers, one limitation to blending is the need to have polymer miscibility in many cases. Much emphasis has been placed on controlling the surface structure of copolymers[5,7,12] because copolymers limit the very large-scale phase separation that occurs in polymer blends that are incompatible. Modification for low-energy surfaces, which provides an opportunity to control properties, adhesion, wetting, dewetting, and mobility, can be achieved by copolymerizing only a small amount of a block component having low surface energy, such as silicon[7,12] or fluorine-containing polymers.[15−22] Although the property and structure of fluorinated polymers with incorporation of fluorocarbons into the polymer backbone[15,16] and on the side chain[17,18] have been extensively investigated, there have been few reports of modification by end group functionalization of short fluorocarbons.[22] DeSimone et al.[22] reported that the surface region of short perfluoroalkyl-terminated polymers was segregated by perfluorinated segments, giving the enhancement of surface perfluorinated segments of 1.6−7.6.

As a class of polymers and copolymers, biodegradable polyesters, based on simple biological acid compounds, such as glycolic or lactic acid, are used, temporarily, as sutures, tissue scaffolding, wound healing, and drug delivery matrices.[9,10,23−26] Although many materials, such as hydrolyzable polyesters and polyanhydrides have been developed in the past decade to improve specific properties, such as biocompatibility, degradability, and drug delivery kinetics, there are still some limitations to their use. To over come this, copolymers with functional side groups to modify the surface with biologically active moieties may be useful.[27,28] However, it may be difficult to control the density of surface functional groups such as hydroxyl or amine groups, due to the surface energy. Our group has investigated the surface functionalization of fluorinated polymers using a radio-frequency glow discharge plasma.[6,8] This surface modification can produce controlled densities of hydroxyl groups on the material surface, and then these groups

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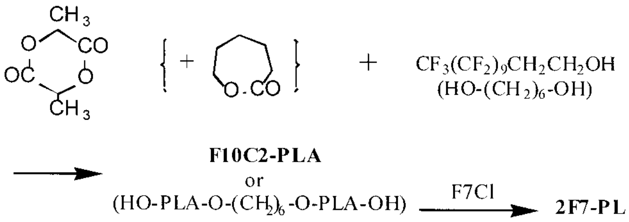
**Scheme 1. Synthesis of Fluorocarbon End-Capped Polyesters**



provide sites for the covalent attachment of a specific component such as proteins or peptides[29,30] and a new approach to controlling surface properties.

We have also extensively studied the factors that control surface segregation in blends and copolymers with a low surface energy component or segment. In the present study, we report the synthesis of polyesters with various lengths of fluorocarbon (F-polyesters) end groups and arms as a new class of materials. The design of the materials is based on principles of surface segregation of a component (in this case the end group) with the lower surface energy. It may be expected that F-polyesters may improve the controllable biodegradability at initial stages by controlling the surface composition of fluorocarbon groups. Cell adhesion may be controlled by adapting plasma and chemical modifications from our previous work[8] to these new fluorocarbon surfaces.

## Experimental Section

**Materials.** L-Lactide and DL-lactide (LA) were obtained from Aldrich and were recrystallized from anhydrous ethyl acetate. Pentadecafluoro-1-octanol (F7C1-OH: the first and the second digits give the carbon numbers of the fluorocarbon and hydrocarbon groups in fluorocarbon alcohols, respectively), 1,6-hexanediol (two arms), pentathrithiol (four arms, Aldrich), and 2-(perfluorodecyl)ethanol (F10C2-OH, Daikin) were dried in a vacuum oven before use. Glycolide (GA, Polysciences), stannous octoate (Sigma), decyl alcohol, pentadecafluorooctanoyl chloride (F7-C1), and heptafluorobutyl chloride (F3-C1, Aldrich) were used as received. All other chemicals were of reagent grade and were used without further purification. For the hydrolytic testing, reagent grade NaOH (Fisher) was used to adjust the pH of the water.

**Polymerization and Functionalization.** Single fluorocarbon-terminated polyesters were directly synthesized by the ring-open polymerization of lactones using with a small amount of hydroxyl-terminated fluorocarbons, F7C1-OH or F10C2-OH, as shown in Scheme 1. Bulk polymerizations were carried out in glass ampules containing a magnetic stirring bar. Stannous octoate in petrolum ether was used as the catalyst for the ring-open polymerization. The ampules were evacuated using a high-vacuum pump and repeatedly flushed with high-purity nitrogen to remove volatile impurities, solvents, and oxygen and then sealed with a blowtorch. The ampules were heated to 130 °C for 1 h, and then the temperature raised to 155 °C. Hexanediol (2F-) and pentaerythitiol (4F-) were used to synthesize multifluorocarbon-terminated polyesters. The synthetic reaction of multifluorocarbon-terminated polyesters is as follows: First, multihydroxy-terminated polyesters were synthesized by the reaction of lactide with hexanediol or pentaerythitiol in vacuum-sealed glass ampules at 135 °C using stannous octoate as a catalyst. Second, the obtained multihydroxyl-terminated polyesters were dissolved in dichloromethane, and a small amount of triethylamine was added. The reactor was cooled to 0 °C in an ice bath. F3-Cl or F7-Cl in dichloromethane was slowly added. The mixture was reacted at 0 °C for 5 h in an ice bath and at room temperature for 40 h. The solution was washed with aqueous NaOH and precipitated in excess of *n*-hexane. The structural characteristics of fluorocarbon end-capped polyesters are shown in Table 1.

**Table 1. Characteristics of Synthesized Fluorocarbon End-Capped Polyesters**

| polymer code | $M_n$ GPC (PDI) | $M_n$ $^1$H NMR | $T_g{}^a$ (°C) | $T_m{}^a$ (°C) |
|---|---|---|---|---|
| L-PLA | 20 000 (2.9) | | 51.0 | 167 |
| F10C2-L-PLA1 | 1 300 (2.2) | | | |
| F10C2-L-PLA14 | 14 000 (1.5) | 3810 | | 156 |
| F10C2-L-PLA29 | 29 000 (1.9) | 11730 | | 167 |
| F10C2-L-LA-*ran*-GA6 | 6 500 (1.9) | | | |
| F7C1-DL-PLA19 | 19 000 (2.9) | 5235 | 35.2 | |
| F7C1-DL-PLA74 | 74 300 (1.7) | | 44.8 | |
| F7C1-L-PLA24 | 24 000 (2.0) | 7568 | | 170 |
| F7C1-L-PLA37 | 37 000 (1.6) | | | |
| F7C1-L-PLA67 | 67 000 (2.2) | | 52.9 | 174 |
| 4F7-L-PLA64 | 64 000 (1.6) | | 50.1 | 170 |
| 2F7-L-PLA25 | 25 000 (2.0) | | 52.5 | 172 |
| F3-L-PLA21 | 21 000 (1.5) | | | |
| 4F3-L-PLA58 | 58 300 (1.5) | | | |

[a] After quenching from 190 °C.

**Bulk Characterization.** The synthesized fluorocarbon end-capped polyesters (F-polyesters) were analyzed by NMR, FTIR, differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), and size exclusion chromatography (SEC). $^1$H NMR spectra were recorded on a INOVA-500 500 MHz spectrometer using deuterated chloroform as a solvent. $^{19}$F NMR spectra were recorded on a INOVA-400 spectrometer at 376.3 MHz, and chemical shifts were referenced to trifluoroacetic acid at −77.5 ppm as a internal standard. FTIR spectra (Perkin-Elmer FTIR 5500 spectrometer) were obtained using a thin film of each sample cast on KBr disks. $M_n$ and $M_w/M_n$ were determined by SEC carried out on samples dissolved in chloroform and eluted with a solvent mixture HFIP/methylene chloride/ chloroform (5/20/75 by wt) at 0.6 mL/min and 25 °C using a set of PLgel columns (500, $10^3$, and $10^4$ Å) and a UV detector. Although the $M_n$ by SEC was different from those from NMR measurements, the SEC data of F-polymers were used in this study. The details of $M_n$ measurements of F-polyesters are the subject of a companion note.[31] The $T_g$ and $T_m$ of F-polyesters including homopolymers were measured by DSC (Perkin-Elmer DSC/TGA 7) under helium, calibrated with pure indium as a standard material. To avoid the effect of residual stress from the sample packing in the aluminum pan and to remove any small traces of solvent, samples were heated to a temperature above 30 °C of $T_g$ or $T_m$ and then quickly cooled to −20 °C. The DSC thermograms were obtained at a heating rate of 20 °C/min. All $T_g$'s were evaluated from the half-height of the heat capacity jump. Also, the thermal stability of F-polyesters was measured by TGA at a heating rate of 40 °C/min under nitrogen.

**Surface Characterization.** The surface chemical compositions of F-polyester films before and after hydrolysis and (F-polyester/-PLA) blend films were obtained using Perkin-Elmer Physical Electronics model 5300 ESCA. Angle-dependent ESCA measurements was performed with an achromatic Mg Kα X-ray source (1253.6 eV) at 15 kV and 20 mA. High-resolution scans of the C 1s, O 1s, and F 1s were acquired at the takeoff angles of 10°, 15°, 30°, and 90°. The polymers were dissolved in methylene chloride to prepare 1% solutions, cast into aluminum weighing dishes, and then allowed to air-dry slowly at ambient temperature. They were further dried in a vacuum oven (ca. 10 Torr) to a constant weight at room temperature. The film thickness was found to be 5 ± 1 $\mu$m.

## Results and Discussion

**Polymer Synthesis.** The surface chemistry of biodegradable polymers will play a major role in defining the nature and extent of the hydrolysis and the biocompatibility within the interfacial region. Fluorinated groups are a very interesting and useful class of materials for surface modifications due to their unique proper-

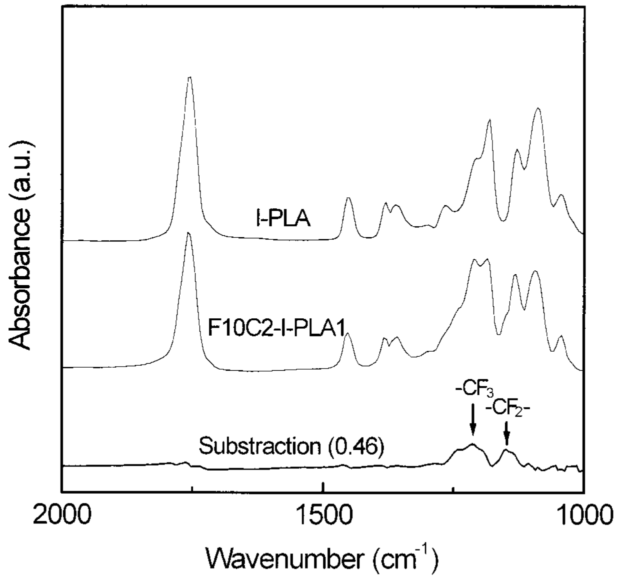


**Figure 1.** FTIR spectra of L-PLA, F10C2-L-PLA1, and their subtraction.

ties such as low surface energy, chemical resistance, and, in some cases, biocompatibility.

It is well-known that the ring-open polymerization of lactones can be initiated by an alcohol using a catalyst.[32] In an attempt to design well-defined surface-functionalized biomaterials, polyesters with different fluorocarbon lengths of 7 and 10 carbons as one side-ended groups were directly obtained by the ionic polymerization of appropriate amounts of lactide, glycolide, or their mixtures and a fluorocarbon chemical having hydroxyl end groups, F7C1-OH or F10C2-OH, in the presence of stannous octoate as a catalyst. For the polymerization of F7C1-polyesters, the reaction was carried out at 130 °C, which is lower than the boiling point of F7C1-OH for 1 h in order to maximize the initial reactivity of lactones with F7C1-OH in a vacuum because at a higher temperature, some F7C1-OH (bp: 162 °C) is in the gas state under vacuum (initial step). After an initial period the temperature was raised to 155 °C for the propagation step. After polymerization for a specific time, the residual monomers, lactones, and impurities were removed by the precipitation of the chloroform-dissolved product in methanol, and the samples were dried in a vacuum oven at 70 °C to remove unreacted fluorocarbon chemicals. For the preparation of the two- and four-arm polyesters with hydroxyl end groups, hexanediol and pentaerythitiol were used, respectively. The reaction sequence is shown in Scheme 1. The degree of polymerization depends on the ratio of lactone concentration to alcohol concentration. Several polymers were synthesized on the basis of the hydroxyl groups as ring-opening reagents and are shown in Table 1. The FTIR spectrum of the F-polymer, F10C2-L-PLA1, along with that of *l*-PLA, is shown in Figure 1. The C=O and the C−F band regions were heavily overlapped, but useful information could be obtained by the subtraction of L-PLA from F10C2-L-PLA1. After subtraction of the spectrum for L-PLA from that of F10C2-L-PLA1, two absorption bands were observed at 1000 and 1100 cm$^{-1}$, corresponding to $CF_3$ and $CF_2$ of fluorocarbon groups, respectively. Figure 2 shows $^1$H NMR and $^{19}$F NMR spectra of F10C2-L-PLA14 in $CDCl_3$. The assignments of the main signals were made by comparison to other work.[33,34] By comparison of the signal intensities of $-CF_2CH_2-$ (F10C2O-; 2.47 ppm) and $-CH-CH_3$ (LA; 5.2 ppm) in the $^1$H NMR, the number-average molecular weight of the F-polyesters can be determined. SEC results for the synthesized F-polyesters, however, are used in this study because the $^1$H NMR peaks of the hydrocarbons linked with fluorocarbons were too small for accurate quantitative integration when the concentration of fluorocarbons in the F-polyesters is decreased. A detailed description of the molecular weight measurement by SEC, NMR, and ESCA is given in ref 31. $^{19}$F NMR assignments for F10C2-L-PLA14 were obtained on the basis of Zhang et al.'s work (Figure 1B).[34]

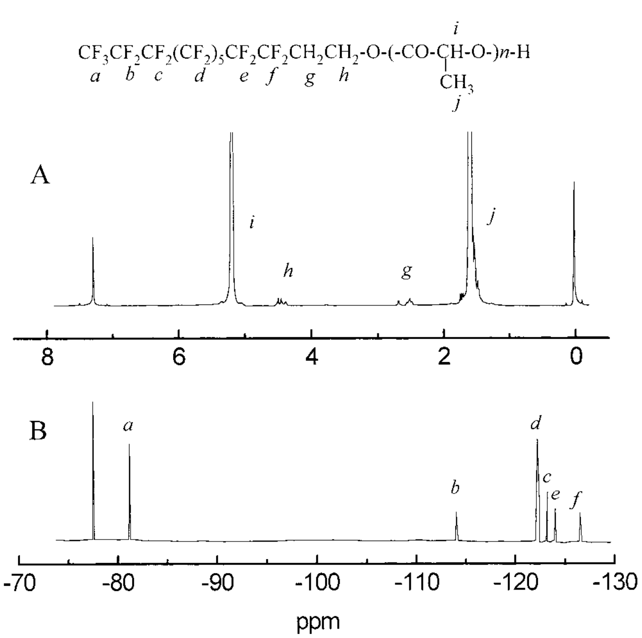


**Figure 2.** $^1$H NMR (A) and $^{19}$F NMR (B) spectra of F10C2-L-PLA14 in $CDCl_3$.

Because of the good thermal stability of fluorocarbon groups, the thermal stability of the obtained F-polyesters should be improved over normal polyesters. Figure 3A demonstrates the TGA results of L-PLA and F-polyesters with different fluorocarbon lengths, F7C1-L-PLA37 and F10C2-L-PLA29. The degradation patterns of the F-polyesters in nitrogen are different from their homopolymer. L-PLA exhibited an onset for degradation around 210 °C while no weight loss was observed at this temperature for the both F-polyesters. As the length (or concentration) of fluorocarbon groups of F-polyesters increases, the thermal stability of F-polyesters is increased. The result of TGA reveals that the F-polyester is quite stable in nitrogen due to the thermal stability of fluorocarbon groups in the bulk and at the surface. Figure 3B compares the DSC curves of L-PLA and F10C2-L-PLA14 at a heating rate of 20 °C/min under flowing helium after preheating to 190 °C and then quickly quenching to −20 °C. In both cases, recrystallization takes place during the heating. From the decrease in $T_g$ and cooling crystallization temperature of F10C2-L-PLA14, it becomes evident that the L-PLA crystalline imperfection due to the relatively high composition of fluorocarbon groups into L-PLA caused a decrease of the L-PLA melting point. The corresponding thermodynamic parameters, including thermal transition temperatures, are shown in Table 2. However, it was observed that the thermal behavior of F-polyesters was similar to that of L-PLA when the $M_n$ of F-polyesters is increased.

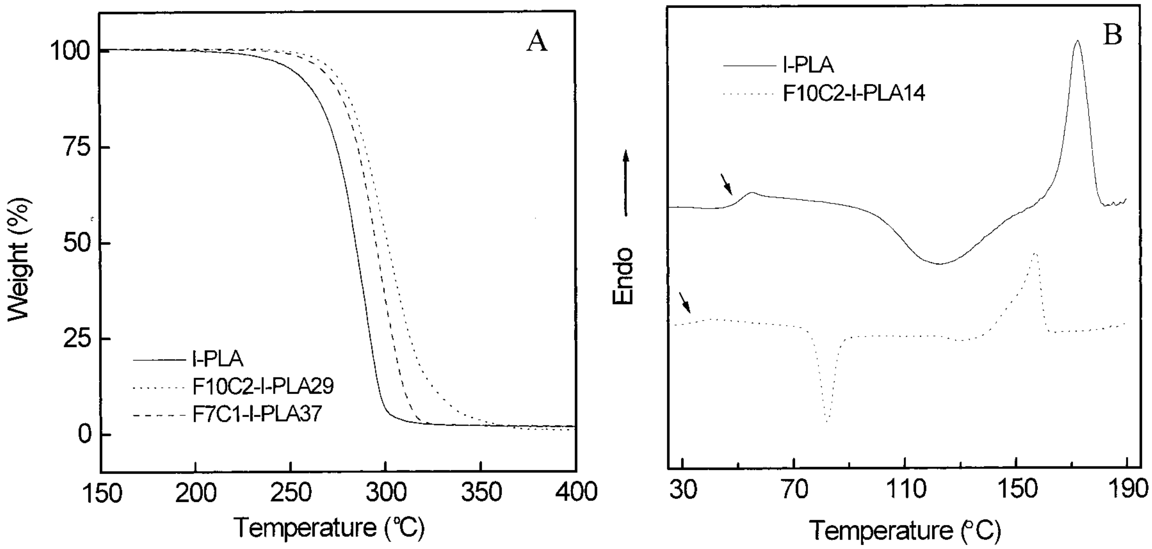


**Figure 3.** TGA (A) and DSC (B) curves of various F-polyesters.

**Table 2. Thermal Transition Temperatures and Thermodynamic Parameters of L-PLA and F10C2-L-PLA after Complete Melting**

| polymer | $T_g$ (°C) | $T_m$ (°C)[a] | $\Delta H_m$ (J/g)[b] | $T_c$ (°C) | $\Delta H_c$ (J/g) |
|---|---|---|---|---|---|
| L-PLA | 51 | 172 | 41 | 118 | −44 |
| F10C2-L-PLA14 | 34 | 156 | 30 | 82 | −20 |
| F10C2-L-PLA29 | 50 | 170 | 44 | 121 | −43 |

[a] $T_m$ is taken at the high-temperature melting peak. [b] $\Delta H_m$ is the sum of the areas under all endothermic peaks.

**ESCA.** As described above, polymers with fluorocarbon end groups can dramatically alter surface properties due to the surface segregation of lower surface energy fluorocarbons. To determine the effect of length of fluorocarbon end groups of F-polyester on the surface composition, angle-dependent ESCA was used. To calibrate the atomic sensitivity factors of carbon 1s, fluorine 1s, and oxygen 1s, ESCA spectra of PLA and poly(vinylidene fluoride) were used. The analytical depth of ESCA was varied by changing takeoff angles between the sample surface and the analyzer of 10°, 30°, and 90°. Figure 4 shows the high-resolution ESCA spectra of C 1s regions of F10C2-L-PLA14 film at various photoelectron takeoff angles. The C 1s region measured at takeoff angle of 90° showed contributions from C−O functional groups at 287.1 eV and O═C−O at 289.1 eV from the PLA and $C-F_2$ at 291.5 eV and $C-F_3$ at 293 eV from the fluorocarbon. From the intensity of the $C-F_2$ fraction (from fluorocarbon) compared to that from O═C−O or C−O (from polyester), the intensity of this peak increases gradually with increasing photoelectron takeoff angle. This suggests that the concentration of fluorocarbon end group is much higher at the topmost surface than at the deeper regions.

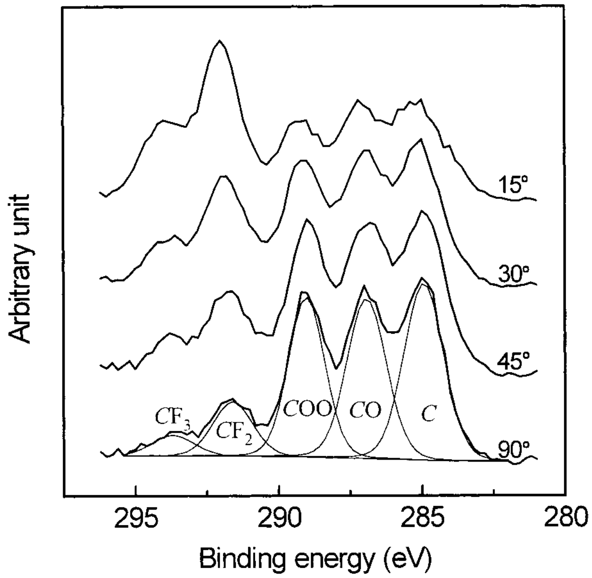


**Figure 4.** C 1s spectra of F10C2-L-PLA14 taken at different takeoff angles.

Usually, there are two ways to evaluate the surface composition from ESCA data: elemental analysis and curve fitting.[35] The ESCA sampling depth depends on both takeoff angle and the kinetic energy of emitted photoelectrons which are excited by the X-ray source. At a particular takeoff angle, therefore, the signals from emitted photoelectrons reflect different sampling depths for each element. In this case, one could use the atomic concentration ratio of fluorine, which can be related to the fluorocarbon group, and oxygen from the polyester because the small amount of fluorocarbon makes the curve fitting in the C 1s region difficult. This approach makes the quantitative analysis of surface composition difficult due to the significantly different sampling depths between fluorine and carbon or oxygen;[36] on the other hand, the signal intensity for C 1s or O 1s will be relatively overestimated, thereby resulting in lower surface composition of fluorocarbon groups than the theoretical one. This result will show the experimental tendency of the surface segregation. From the F 1s/O 1s area ratio of F10C2-PLA it is possible to calculate the ratio of each unit at the surface region using following equation:

$$\frac{I_{\mathrm{F\,1s}}}{I_{\mathrm{O\,1s}}} = \frac{21}{2n} \tag{1}$$

where $n$ is the average number of lactide repeating unit per fluorocarbon group; 21 and 2 reflect numbers of the fluorine in a fluorocarbon group and the oxygen of lactide repeating unit, respectively. Figure 5 shows the ratio of lactide unit to fluorocarbon unit calculated by

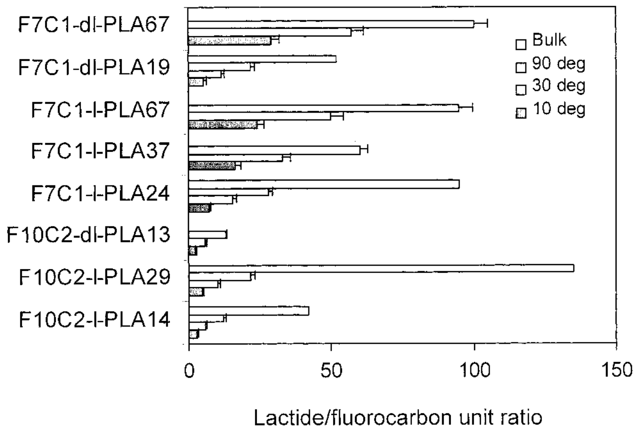


**Figure 5.** Unit ratio profiles of various fluorocarbon end-capped polyesters.

eq 1. In bulk, *n* of F7C1-DL-PLA19 is much lower than that of F10C2-L-PLA24; that is, the concentration of fluorocarbon groups in F7C1-DL-PLA19 is higher than that of F10C2-L-PLA24, but angle-dependent ESCA results are very similar to each other. This means that the longer the fluorocarbon group, the higher the surface fluorocarbon concentration, as expected; that is, the extent of surface segregation of the fluorocarbon group strongly depends on the length of fluorocarbon, as well as the bulk composition.

As found in many blend systems, the surface composition in multicomponent systems containing small amounts of specific materials is dramatically different from the bulk composition due to surface segregation which minimizes the surface energy. To prevent the large-scale phase separation between blend components due to their incompatibility, which induces the poor physical and mechanical properties, a typical approach is to blend an AB block copolymer with the B homopolymer.[7,12] When the concentration (or length) of A block acting as a surface-active component is much lower than that of B block in the copolymer, for example, fluorocarbon (A) end-capped polyester (B), a homogeneous mixture occurs at the interface between blend components because the B block will be serve to the anchor B homopolymer as a matrix. Therefore, the A block segregates to the surface while the bulk is composed of the B component. Then the A surface layer will produce a barrier between air and the B component. Therefore, blending a biodegradable polyester with a functionalized polyester, F-polyester, can also provide the potential to fabricate new materials to design biodegradable polymer devices with controllable hydrolytic kinetics in the initial degradation stage. The surface segregation of fluorocarbon groups produced a barrier between the polyester and the hydrolyzing solution. Hence, the kinetics of initial hydrolytic degradation are determined by the degree of surface segregation of fluorocarbon end groups. Figure 6 shows the influence of F10C2-L-PLA composition in the F10C2-L-PLA/L-PLA blend on the surface composition of fluorocarbon groups. The F 1s/O 1s ratio is proportional to the composition of F10C2-L-PLA in the blend. This result indicates that the control of the surface fluorocarbon concentration by changing the blend composition gives a biodegradable material with the desired initial retardation time for the degradation.

**Hydrolysis.** Taking the advantage of the property of fluorocarbons, such as surface segregation and water resistance, F-polyesters make them or their blends useful for the retardation of degradation as biomaterials because the surface segregation of the fluorocarbon component in the F-polyesters causes the resistance to water permeation into the bulk. At the initial stage of hydrolysis, therefore, the decrease of fluorine concentration will be observed due to the surface erosion. Since ESCA is a useful tool to probe the surface composition of multicomponent systems, it might be possible to estimate the relative degradation rate from the change of the surface composition of F-polyesters as a function of hydrolysis time. Figure 7 shows C 1s spectra of F10C2-L-PLA29 at takeoff angle of 30° as a function of hydrolysis time at pH = 11.7. The intensity of $CF_2$ decreases progressively with increasing the hydrolysis time. This result can be explained by the fact that the fluorocarbon groups at the surface are removed due to the hydrolysis of ester groups adjacent to fluorocarbon groups. Figure 8 shows atomic ratio profiles of F7C10-L-PLA67 and F10C2-L-PLA29 films after hydrolysis at pH = 11.7. In both cases, the F 1s/O 1s ratio is

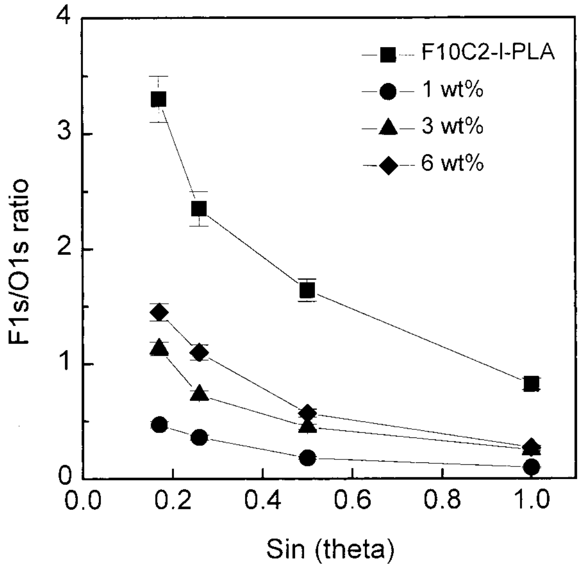


**Figure 6.** Surface atomic ratio profiles of (F10C2-L-PLA14/L-PLA) blend films.

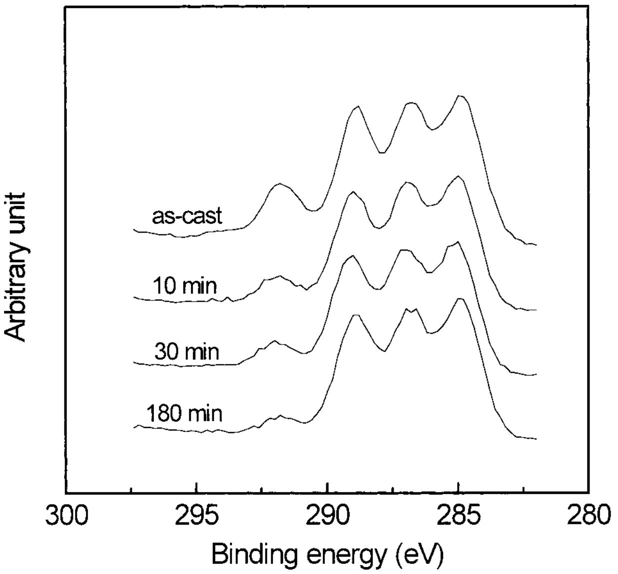


**Figure 7.** C 1s spectra of F10C2-L-PLA29 measured at a takeoff angle of 30° as a function of hydrolysis time at pH 11.4.

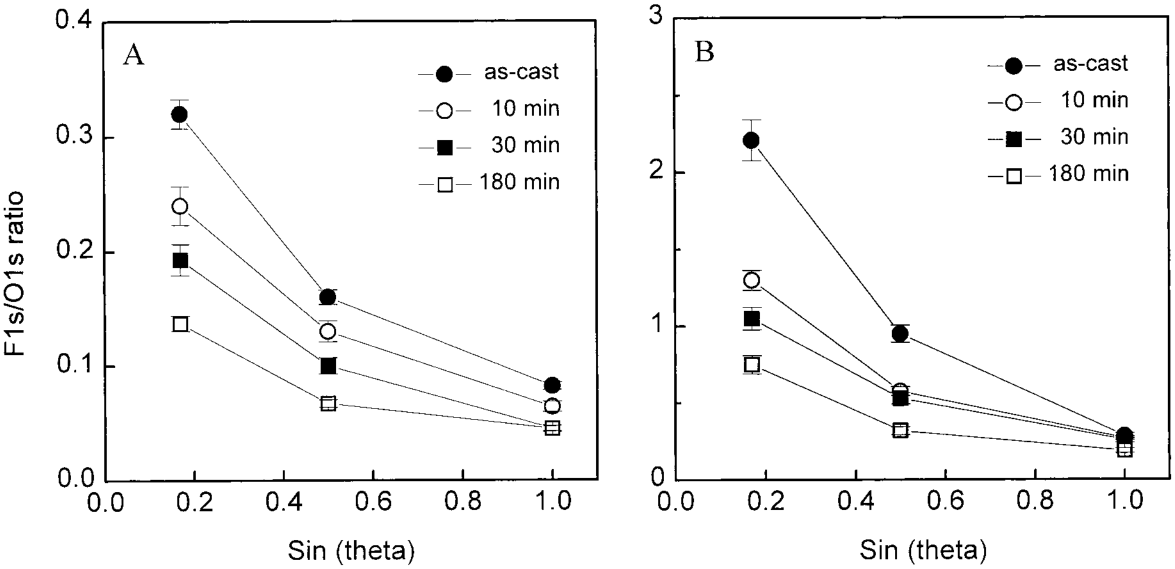


**Figure 8.** Atomic ratio of F 1s/O 1s vs sampling depths profiles of F7C1-L-PLA67 (A) and F10C2-L-PLA29 (B) as a function of hydrolysis time at pH 11.4.

progressively decreased as the hydrolysis time is increased. While the F 1s/O 1s ratio of F10C2-L-PLA29 film is more sharply decreased than that of F7C10-L-PLA67 at the initial hydrolysis time, the relative variation of F10C2-L-PLA29 film at photoelectron takeoff angle of 90° is much smaller than that F7C10-L-PLA67 as the hydrolysis time is increased. As described above, the surface segregation of fluorocarbon groups in F10C2-L-PLA29 is much higher than that of F7C10-L-PLA67 at the topmost surface. This result might indicate that fluorocarbon groups at the topmost surface are removed by hydrolysis. In other words, the surface erosion of fluorocarbon groups in the F10C2-L-PLA29 due to the hydrolysis takes place in the topmost layer. The F 1s/O 1s ratio is much sharply decreased at takeoff angle of 15° after 10 min of hydrolysis time, and then there is no significant change at takeoff angle of 90°. Thus, the increased segregation of F10C2- end groups, due to the longer fluorocarbon chain, proves to be more effective at resisting hydrolysis of the PLA component. This provides a surface barrier to hydrolysis created by segregated fluorocarbon groups.

## Summary

A series of fluorocarbon end-capped polyesters were synthesized on the basis of the ring-open polymerization of lactones initiated by an alcohol. The effect of fluorocarbon end group length on the surface structure of the F-polyesters before and after hydrolysis and its blend with polyesters was investigated by ESCA. Angle-dependent ESCA measurements show that the dominant factors in defining the surface composition of F-polyesters are fluorocarbon chain length and molecular weight, not bulk composition. With a similar F/O ratio, a longer fluorocarbon length gives a surface richer in fluorocarbon. These synthesized F-polyesters, therefore, will show the property of retarded initial degradation rate dominated by the fluorocarbon chain chemistry, surface segregation, and water repellency. The surface modifications of F-polymers and its blends by plasma treatments are presently under investigation in order to give F-polymer surfaces reactivity with proteins or peptides.

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