Communications

Synthesis and Surface Structure of Polyester-*block*-Poly(dimethylsiloxane)-*block*-Polyester Copolymers

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Abstract: Triblock copolymers of poly(dimethylsiloxane) (PDMS) middle block and degradable polyester end blocks were synthesized by the ring open polymerization initiated by alcohol groups of PDMS. Surface composition of the triblock copolymers is measured by angle-dependent electron spectroscopy for chemical analysis. The PDMS blocks are segregated in the topmost surface region and constituted up to 90 mol% of the surface, even though the overall bulk PDMS concentrations of the block copolymers is 6% or less. This result suggests that the bulk property of degradable polyesters is essentially unchanged due to the high surface segregation of PDMS.

Keywords: poly(dimethylsiloxane), electron spectroscopy for chemical analysis, surface segregation.

Introduction

In some polymeric systems, the surface composition differs, sometimes dramatically, from the bulk composition, resulting in a material with distinct surface properties, such as bioadhesion or wettability. It has been well known that the component of a lower surface free energy in multicomponent polymeric systems are preferentially concentrated at the air surface region in order to minimize the air/material interfacial free energy.[1-11] A desired polymer surface, sometimes cannot be obtained from the material itself but through chemical or physical modification. The most common surface modification techniques include blending,[5,11] copolymerization,[6,7,10] chemical surface reactions,[3] flame treatment,[2] and plasma treatment.[1,6,12] Some conventional polymers with low surface energy are poly(tetrafluoroethylene) (18 mN/m) and poly (dimethylsiloxane) (PDMS) (22 mN/m).[13]

The outstanding properties of PDMS make them broad application in industrial areas for the bulk and surface modification of polymeric system. Some of the most interesting properties of PDMS include extremely low glass transition temperatures, biocompatibility, hydrophobicity, and low surface energy.[4-6,14] Despite their unique properties, pure PDMS has too weak mechanical property to be used directly and shows the thermodynamic incompatibility with most other polymers due to its low solubility parameter. Therefore, most efforts in the use of PDMS for surface modification have dedicated to the synthesis of siloxane-containing multicomponent polymeric systems, block or graft copolymers or its blends. This paper describes the synthesis and the surface characterization of ABA type siloxane-containing block copolymers where the middle block is PDMS and both end blocks are biodegradable polyesters, poly(lactide) (PLA), lactide-*co*-caprolactone (LA-*co*-CL), or lactide-*co*-glycolide (LA-*co*-GA).

Experimental

Reagents. *l*- and *dl*-lactides were obtained from Aldrich and recrystallized from anhydrous ethyl acetate. Glycolide (Polysciences), ε-caprolactone (Aldrich), and stannous octoate (Sigma) were used as received. Hydroxy-termeinated PDMS (HO-PDMS-OH, M_n = 1,000, boiling temperature = 147 °C) was purchased from Aldrich. All other chemicals were reagent grade and used without further purification.

Polymerization. ABA types, polyester-*b*-PDMS-*b*-polyester copolymers, were obtained by the ring open polymerization of lactones in the presence of HO-PDMS-OH as a middle block. The bulk polymerization was carried out in a vacuum-sealed glass ampoule with a magnetic bar at a given temperature using 0.5 wt% of stannous octoate as a catalyst. In order to control the T_g of both end polyester blocks in a triblock polymers, the mixtures of LA and CL or GA mono-

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mers were used. Copolymerization reactions were completed in two steps as shown in Scheme I. The first step (initiation) was conducted at 110-130 °C in order to increase the initial reactivity of HO-PDMS-OH because HO-PDMS-OH has the boiling temperature of 147 °C and then will be the gaseous state in vacuum at a high temperature. The second step, propagation, was performed at 155-160 °C for certain time. The final products in the ampoules were dissolved in chloroform and precipitated with excess of methanol and then washed with n-hexane in order to remove unreacted PDMS oligomers.

Bulk Characterization. Average molecular weight and polydispersity of the ABA type block copolymers were determined using gel permeation chromatography (GPC) with a Waters system (Waters 510) consisting of a 515 precision pump on the basis of polystyrene calibration curve. Copolymer composition and block length of the ABA type block copolymers were confirmed by ^{1}H-nuclear magnetic resonance (NMR) spectroscopy (INOVA-500, 500 MHz, CDCl$_3$). The molecular characteristics of the copolymers synthesized in this study are listed in Table I. dl-PLA-b-PDMS2 indicates that both end blocks in the triblock copolymer are dl-PLA and the number is the mole fraction of PDMS in the copolymer. The T_g of the synthesized triblock copolymers was

PLA-b-PDMS-b-PLA

or

LA-ran-CL-b-PDMS-b-LA-ran-CL
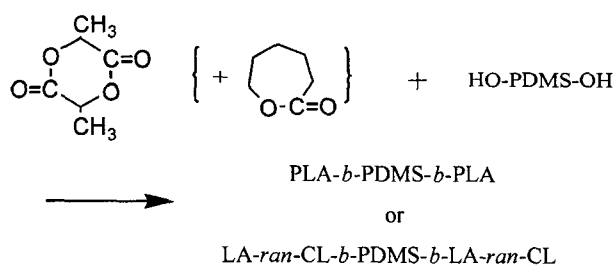
Scheme I. Synthesis of polyester-b-PDMS-b-polyester triblock copolymers.

measured by differential scanning calorimeter (DSC) (Perkin-Elmer DSC/TGA 7) calibrated pure indium as a standard. The DSC thermograms were obtained at a heating rate of 20 °C/min. The T_g was determined as the half-height on the heat jump. Also, the thermal stability of the triblock copolymers was measured by thermogravimetric analyzer (TGA) at a heating rate of 40 °C/min.

Electron Spectroscopy for Chemical Analysis (ESCA). The surface chemical compositions of the triblock copolymers were evaluated on the basis of ESCA (Perkin-Elmer Physical Electronic Model 5100 ESCA) using MgKα X-ray source operation at 5 kV and 20 mA. An operating pressure was not higher than 5×10^{-8} torr. A pass energy of 89.45 eV was used for the survey spectra and 35.75 eV was used for multi-region scans. High-resolution scans were obtained at the take-off angles of 15°, 45°, and 90°. The corresponding depths of C1s were 27, 73, and 103 Å^2, respectively. Recalibration of atomic sensitivity factor ratio was made according to the method previously reported.[15] Films for ESCA measurements were cast from 1% chloroform solution (w/ v) on aluminum weighing dishes. The films were dried in air slowly and then kept in a vacuum oven to keep constant weight at room temperature.

Results and Discussion

Copolymerization. It is well known that the ring open polymerization of lactones can be initiated by a hydroxyl group using a catalyst.[10] In an attempt to design well defined surface-functionalized biomaterials, triblock copolymers were directly obtained by the ionic polymerization of appropriate amounts of lactide, glycolide, or their mixtures and PDMS having hydroxyl end groups in the presence of stannous octoate as a catalyst. The propagation reaction consists of steps-wise addition of the lactone to the hydroxyl group. The use of HO-PDMS-OH as an initiator results in a poly-

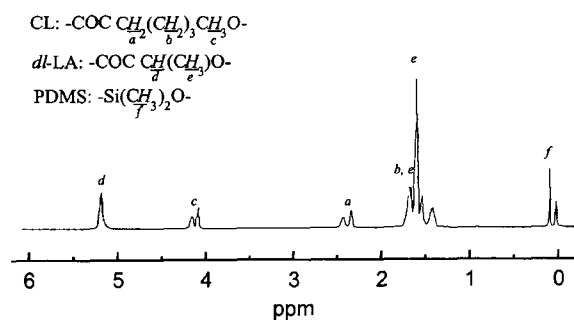**Table I. Characteristics of Synthesized Triblock (A-B(PDMS)-A) Copolymers**

Polymer	Polym. Comp. (mol %)[a]	Yield (%)	M_n (g/mole) (PDI)	$T_g{}^b$ (°C)	T_m (°C)	Block Length
dl-PLA-b-PDMS2	dl-LA/DMS 98/2	70	35,000 (2.5)	40	-	-
dl-LA-ran-CL-b-PDMS1^c	dl-LA/CL/DMS 87.5/11.6/0.9	74	67,000 (1.7)	10	-	(CL) 1.53
dl-LA-ran-CL-b-PDMS5^c	dl-LA/CL/DMS 88.8/6.7/4.5	73	34,000 (2.3)	26	-	(CL) 1.41
dl-LA-ran-GA-b-PDMS1	dl-LA/GA/DMS 71.3/27.5/1.2	42	6,400 (2.1)	43	-	(GA) 1.57
l-PLA-b-PDMS7	l-LA/DMS 93.5/6.5	36	78,000 (1.5)	-	180	-
l-LA-ran-CL-b-PDMS4	l-LA/CL/DMS 72/24.3/3.7	68	33,000 (2.3)	6	-	(CL) 2.19

[a] Measured by ^{1}H-NMR. [b] Determined by the half-height on the heat jump (after pre-heating to 120 °C in order to avoid thermal history).
[c] The number indicates the mole fraction of DMS unit in the copolymer.

ester-PDMS-polyester triblock copolymer with hydroxyl end groups. The composition of each block or the degree of polymerization was influenced by the reaction temperature and the feed ratio of lactone to hydroxyl group. Several PDMS triblock copolymers were synthesized. To control the T_g of polyester block, appropriate amount of mixtures of lactide with caprolactone or glycolide were used. The resulting triblock copolymers were characterized by ^{1}H-NMR, infrared spectroscopy, GPC, TGA, and DSC. ^{1}H-NMR was used to confirm the composition of PDMS and the block length of the copolymers. Figure 1 shows the chemical structures and the ^{1}H-NMR spectrum of *dl*-LA-*co*-CL-*b*-PDMS5. The mole fractions of each monomeric unit were determined from the intensity ratio of -C*H*- proton resonance of LA at 5.2 ppm (and -C*H*$_2$-O- proton resonance of CL at 4.1 ppm) to C*H*$_3$-Si- proton resonance of PDMS at 0.08 ppm. From these ratios dimethylsiloxane contents in the triblock copolymers were from 0.9 to 6.5 mol%. Also, the block length of each component of LA-*co*-CL was calculated from the ratio of CL-LA to CL-CL segments of -CH$_2$-O- proton resonance region of CL. This result indicates that the polyester block, composed with two components, is a random structure. The thermal behavior of the synthesized copolymers was examined by DSC. All copolymers except *l*-PLA-*b*-PDMS had no melting endotherms because of a random structure of polyester blocks. The measured physicochemical properties synthesized in this study are shown in Table I.

Surface Composition. To evaluate the surface structures of the various triblock copolymers synthesized, angle-dependent ESCA measurements were performed. High resolution C1s and O1s spectra of *dl*-LA-*co*-CL-PDMS1 measured at a takeoff angle of 90° are shown in Figure 2. According to the architecture of the triblock copolymers, the C1s region of all copolymers can be deconvoluted with three peaks at 285, 287.5, and 289.5 eV assigned to that correspond to the neutral carbon (-*C*-), ether carbon (-*C*-O-), and carbonyl carbon (-O-*C*O-), respectively. The neutral carbon peak in the C1s region reflects the contributions of both the polyester and PDMS blocks while the other are just due to the ester bond of polyester blocks. Also, the O1s spectra can be fitted
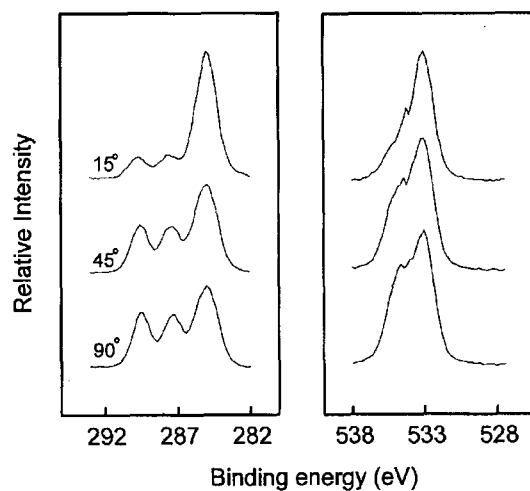
by two peaks which can be assigned to the oxygen of the polyester and the PDMS blocks as assigned in Figure 3 while the Si2p region of all triblock copolymers shows a singlet symmetrical peak from the PDMS block.

Figure 3 shows the C1s and O1s core-level spectra, obtained at three takeoff angles of 15°, 45°, and 90° for *dl*-LA-*ran*-GA-*b*-PDMS1. As mentioned above, the two small symmetric peaks at 287.5 and 289.5 eV in the C1s region (in the case of O1s region, the shoulder at a higher binding energy) are characteristic of the polyester block. In both C1s and O1s regions, the peak intensities of the polyester block increases progressively with increasing photoelectron takeoff angle. This suggests that the concentration of polyester is lower at the topmost surface than in the deeper surface, while the concentration of PDMS exhibits the opposite trend. The surface energy of PDMS is much lower than those of polyesters (40-42 mN/m, calculated on the basis of the additive rule[13]), the surface region of the polyester-PDMS-polyester block copolymer film is expected to be rich in
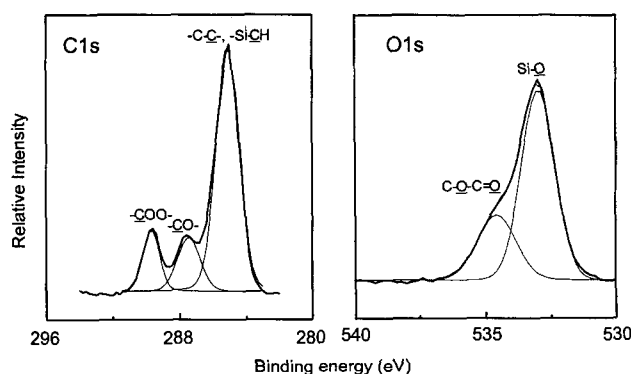
Figure 2. Curve-fitted spectra of the *dl*-LA-*ran*-CL-*b*-PDMS1 triblock copolymer measured at 45° of takeoff angle.

CL: -COC C*H*$_2$(C*H*$_2$)$_3$C*H*$_2$O-
         a   *b*   *c*

dl-LA: -COC C*H*(C*H*$_3$)O-
           d   *e*

PDMS: -Si(C*H*$_3$)$_2$O-
          f

Figure 1. ^{1}H-NMR spectrum of *dl*-LA-*ran*-CL-*b*-PDMS5 in CDCl$_3$.

**Figure 3.** ESCA spectra of *dl*-LA-*ran*-GA-*b*-PDMS1 triblock copolymer with different takeoff angles.

PDMS component at the air side in order to minimize the total free energy of the copolymers.

Usually, there are two ways to evaluate the surface composition from ESCA data, elemental analysis and curve fitting. 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 silicon to carbon in order to calculate the surface composition because the sampling depths of C1s and Si2p are very close: for Mg Kα X-ray source at a 90° takeoff angle, 102.7 and 112 Å, respectively.

Figure 4 illustrates the surface mole fraction of PDMS for various synthesized copolymers measured by angle-dependent ESCA. The atomic ratios of carbon and silicon were used in the quantitation. According to the structures of the repeating units of polyester and PDMS, the surface DMS mole fraction, X_{DMS} of dl-PLA-b-PDMS is expressed in the terms of the Si/C atomic ratio as

$$\frac{Si}{C} = \frac{X_{DMS}}{3(1-X_{DMS})+2X_{DMS}} \tag{1}$$

in which Si and C are the atomic percentages of silicon and carbon from ESCA measurements, respectively. As shown in this figure, the surface region of all the copolymers is dominated by PDMS. The highest PDMS mole fraction at the surface (here, l-PLA-b-PDMS) is 0.93, not 1 as reported previously for some PDMS copolymers, even though the bulk PDMS concentration is as high as 6.5 mol%.[6] This can be explained by small molecular weight of PDMS block used in this study, approximately 1,000 g/mole. Therefore, these materials will be useful for the control in the biocompatibility and the biodegradability due to the surface segre-
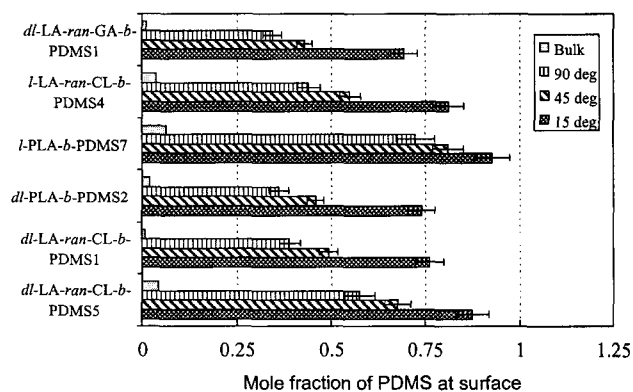
Figure 4. PDMS surface concentration profiles of various triblock copolymers.

gation of PDMS with unique properties.

Conclusions

In this study, a series of polyester-PDMS-polyester triblock copolymers was synthesized using the ring open polymerization technique initiated by an alcohol as a surface-functionalized biomaterial for medical applications on the basis of the unique properties of PDMS, such as low surface energy, very low T_g, and biocompatibility. Quantitative angle-dependent ESCA was used to investigate the surface enrichment. Angle-dependent ESCA measurements show that the dominant factors in defining the surface composition are bulk content and chain length of PDMS in the copolymer. As expected, the surface enrichment of PDMS was obtained, depending on the concentration of PDMS in the copolymers.

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