

Growth of Monolayered Poly(*l*-lactide) Lamellar Crystals on a Substrate

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Abstract: Hydroxyl groups were introduced onto the surface of a silicon wafer by O₂ plasma treatment. Poly(*l*-lactide) (*l*-PLA) was attached onto the surface-modified silicon wafer by the ring-opening polymerization of *l*-lactide using the hydroxyl group as an initiator. Lamellar single crystals of *l*-PLA were grown directly on the *l*-PLA-attached silicon wafer from a 0.025% solution in acetonitrile at 5 °C. A well-separated, lozenge-shaped, monolayered lamellar single crystal was prepared because the *l*-PLA-attached silicon wafer acts as an initial nucleus.

Keywords: plasma treatment, poly(*l*-lactide), single crystal.

Introduction

Degradable polymers are of growing interest in the areas of biomedical applications and polymer waste management caused by synthetic non-degradable polymers.¹⁻⁶ Polymer degradation occurs primarily in the hydrolyzable backbone linkages of the polymer chain, leading to a lower molecular weight and eventually to monomer regeneration. Well-known hydrolyzable polymers are polysaccharides,¹ polyesters,^{2,7} poly(amino acids),² and polyanhydrides.⁸

It is well known that poly(*l*-lactide) (*l*-PLA) is a biodegradable and biocompatible crystalline polymer. Degradability of PLAs has been widely investigated for their commercial biotechnological applications, controlled-release devices in the areas of biomedical devices and disposable degradable plastic articles because of their nontoxic products in metabolism caused by hydrolytic chain scission, eventually leading to lactic acid.^{3,4,9,10} High molecular weight PLAs which show suitable mechanical properties for applications can be obtained by ring-opening polymerization of cyclic diesters.⁹

Although various factors can affect the degradation behavior of aliphatic polyesters, the morphology plays a critical role in degradation phenomena.³ The degradation of semicrystalline polymers starts in the amorphous regions and then hydrolytic attack progresses within the crystalline regions. To study a degradation behavior in the crystalline region, the chain-folded solution-grown lamellar crystals of

hydrolyzable polymers have been used as a model system.^{4,5} *l*-PLA lamellar single crystals have been prepared from several solvents by an isothermal crystallization and shows two kinds of crystal morphologies, lozenge-shaped and hexagonal-shaped lamellar crystals with spiral growth.^{4,11,12} Recently, Iwata and Doi determined the reciprocal lattice parameters of both *l*-PLA crystals $a = 0.935 \text{ nm}^{-1}$, $b = 1.626 \text{ nm}^{-1}$, and $\gamma = 90^\circ$.⁴ However, most prepared *l*-PLA single crystals showed multi-lamellar or stacked morphology. This sometimes makes measurements of their physical properties difficult. Here, we report the new preparation of a monolayered *l*-PLA lamellar crystal on a substrate for the first time.

Experimental

Materials. *l*-PLA ($M_w = 72 \text{ k}$, $M_w/M_n = 1.7$) was synthesized by ring opening polymerization of *l*-lactide using stannous octoate as a catalyst. It is well known that the ring opening polymerization of *l*-lactide can be initiated by an alcohol using a catalyst.⁹ Polymerization of *l*-LA was performed on hydroxyl group-functionalized substrates such as slide glass and plasma-treated silicon wafer.

For this work, the surface of silicon wafer was partially hydroxyl functionalized by radio frequency glow discharge treatments in a plasma chamber (SMACO RIE system 10NR). The chamber had a base pressure below 10 mTorr, which was achieved by mechanical and oil diffusion pump. The sample chamber was purged with modification gas, O₂ for 10 min at 200 mTorr using a flow rate of 200 L/min

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before initiating plasma treatment. The operating pressure of the plasma was 200 ± 10 mTorr. The O_2 was introduced into chamber through an ultrahigh vacuum leak valve for the formation of hydroxyl groups.¹³ The plasma condition involved 5 sec of plasma exposure time at a 200 W power level. A partial hydroxyl-functionalized silicon wafer was used as prepared in this way.

Preparation of Solution-grown Crystals. The single crystals of *l*-PLA were grown from acetonitrile dilute solution. *l*-PLA (0.5 mg) was dissolved into 10 mL of acetonitrile at 80 °C which contained slide glass and plasma-treated silicon wafer. The solution was slowly cooled to room temperature and kept in a refrigerator at 5 °C for 24 h. Both substrates were taken out and carefully washed with methanol several times.

Microscopic studies. Atomic force microscopic measurements were conducted using a scanning force microscope, SPA 300 instrument with SPI 3700 controller (Seiko Instrument Co.) at room temperature. The cantilever used in this study was triangular with a microfabricated Si_3N_4 microtip (Olympus Co.), and a spring constant of 0.022 N/m. The scanning direction was perpendicular to the long axis of the cantilever. Topographic image was carried out in the repulsive force region (ca. 1 nN).

Transmission electron microscopic study was performed on JEM-2000FX II electron microscope operated at acceleration voltages of 200 kV for the electron diffraction diagrams and 120 kV for imaging of shadowed crystals. Solution-grown crystals were placed on carbon-coated grids and allowed to dry and then shadowed with Pt-Pd alloy. Electron diffraction was measured without shadowing.

Results and Discussion

Lamellar single crystals of aliphatic polyesters, grown from a dilute solution by an isothermal crystallization method, are intramolecular crystals which have well defined structures. Thus, lamellar single crystals are very useful model substrates to elucidate the mechanism of enzymatic or hydrolytic degradation on the crystal regions.³⁻⁵ Usually, lamellar single crystals of polymeric materials have been prepared from a dilute solution: a polymer is dissolved into an excess of solvent at a high temperature and the solution is isothermally crystallized at a low temperature. In this method, there is a possibility of undesirable growth of crystals during the separation process by centrifugation. Also, the obtained lamellar crystals usually showed a spiral or stacked morphology. Our previous study showed that the substrate-supported poly [*R*]-3-hydroxybutyrate single crystals provide better opportunities to observe the morphological changes caused by degradation.⁵ It is because the crystals attached to a substrate can minimize some small fragments that come off during washing and separation.

The shape of a crystal is fundamentally related to the molecular packing. It should be noted, therefore, that even if crystals grow from the same solvent, the crystals might have different shapes due to different crystal structures. Besides the temperature, cooling rate, concentration, and solvent, the substrate on which the crystal is growth can also affect its morphology. At the same time, many crystals are nucleated and grow on the walls of solution vessel or immersed substrate, such as a slide glass and mica, although the crystals are nucleated and grown in the solution.¹⁴ Here, a new preparation method of *l*-PLA single crystals was applied: *l*-PLA was directly polymerized on the substrates because the ring-opening polymerization of *l*-lactide can be initiated by an alcohol using a catalyst. This *l*-PLA-attached substrate can play initial nucleuses. *l*-PLA-attached substrates were placed in 0.01% (w/w) acetonitrile solution and heated to 80 °C. The *l*-PLA crystals grew at an isothermal crystallization. Since a slide glass itself and *l*-PLAs are good nucleating surfaces,¹⁴ the *l*-PLA-attached slide glass was used for preparing aggregated multilayered lamellar crystals. A crystallization time of *l*-PLA-attached slide glass was much longer than that of *l*-PLA-attached silicon wafer. After the crystallization, the substrates were taken out from the solution and carefully washed with methanol. This process can prevent an undesirable growth of crystals. To conform the crystal structure, some crystals, which are grown in the solution and adhered to the *l*-PLA multilayered lamellar crystals grown on the *l*-PLA-attached slide glass for long time, were separated by slow immersion into water. The floating crystals were deposited on carbon-coated grids. Typical electron micrograph and electron diffraction pattern of lozenge-shaped single crystals of *l*-PLA are shown in Figure 1. The angles between growth faces are ca. 60 and 120°. The characteristic feature of the diffraction pattern is that the 110 and 200 reflections are very strong with a highly ordered pattern. All of the reflections can be indexed as $hk0$ reflections based on the orthogonal unit cell reported previously,¹² like a flat lamellar polyethylene crystal.¹⁵

To control the surface concentration of hydroxyl groups of

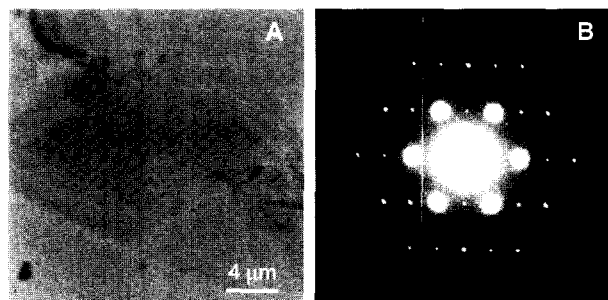


Figure 1. Electron micrograph (A) and typical electron diffraction pattern (B) of *l*-PLA single crystals grown on the *l*-PLA-attached slide glass.

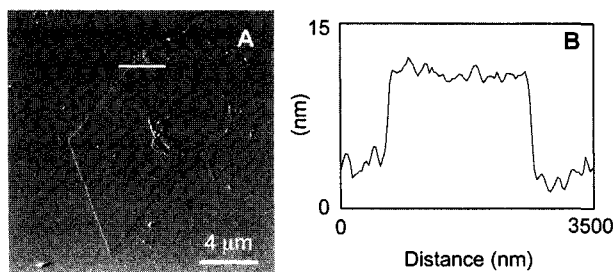


Figure 2. AFM topographic image (A) and line profile data (B) of *l*-PLA single crystals grown on the *l*-PLA-attached silicon wafer.

substrates, plasma treatments were applied to silicon wafer. The methods of plasma treatments and polymerization were described in the Experimental Section. Although the concentration of surface hydroxyl groups cannot be measured, a short exposure time of O₂ plasma may produce low surface concentration of hydroxyl groups.¹³ The surface polymerization and crystal growth were conducted in the same solution as before, except crystallization time. Figure 2 shows AFM topographic image of a *l*-PLA single crystal grown onto the *l*-PLA-modified silicon wafer and line profile data. The *l*-PLA single crystal on the modified substrate occurs as a well separated monolayered lamellar lozenge-shaped crystal with a side of 7 μm. The measurement of the thickness yields value of around 12 nm. The formation of monolayered crystals is supported by the fact that the crystals nucleated on a substrate apparently are constrained to grow on the substrate and develop as flat lamellae.¹⁴ Further studies concerning the enzymatic and hydrolytic degradations using the monolayered lamellar crystal of *l*-PLA are now in progress.

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