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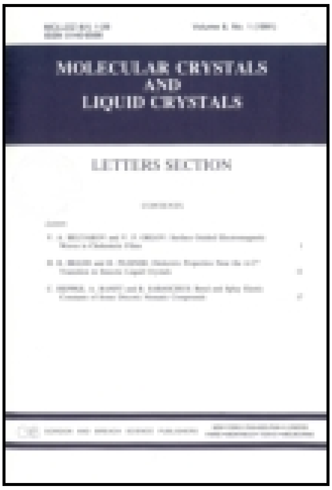

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Morphological Study on Mechanical Deformation and Alkaline Hydrolysis of Solution-Grown Poly(l-lactide) Crystals

Nam-Ju Jo[a], Ildoo Jung[a], Seong Soo Park[b], Won-Ki Lee[b] & Chang-Han Lee[c]

[a] Department of Polymer Science & Engineering, Pusan National University, Busan, Korea

[b] Division of Chemical Engineering, Pukyong National University, Busan, Korea

[c] Department of Environmental Administration, Catholic University of Pusan, Busan, Korea

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Morphological Study on Mechanical Deformation and Alkaline Hydrolysis of Solution-Grown Poly(l-lactide) Crystals

NAM-JU JO,[1] ILDOO JUNG,[1] SEONG SOO PARK,[2]
WON-KI LEE,[2,*] AND CHANG-HAN LEE[3]

[1]Department of Polymer Science & Engineering, Pusan National University, Busan, Korea
[2]Division of Chemical Engineering, Pukyong National University, Busan, Korea
[3]Department of Environmental Administration, Catholic University of Pusan, Busan, Korea

Biodegradable poly(l-lactide) (l-PLA) solution-grown crystals (SGC), which are the lozenge-shaped morphology of unique dimension with one side of 12 μm, were grown from dilute solution of acetonitrile. Morphological changes by alkaline degradation and mechanical deformation of PLLA SGC were investigated by atomic force microscopy. Although their enzymatic degradation did not show the change of molecular weight, alkaline hydrolysis of the crystals showed strong fragment of small molecular weights. The mechanical deformation of crystals on PET film by elongation showed the microcracks which were almost perpendicular to the elongation direction. These results indicate that alkaline hydrolysis at initial stage occurred in the chain-folding surface and the remained chains were rapidly eroded in small lozenge shape.

Keywords Poly(l-lactide); solution-grown crystals; alkaline hydrolysis

Introduction

An increase in environmental concerns about petroleum-based polymers has led to growing interest in bio-based polymers. Among them, poly(lactide) (PLA) is one of the most promising biodegradable polymers derived from bio-based resources, fermented plant starch and sugars, owe to its mechanical property, processability, and biodegradability. Degradation behaviors of PLA by enzyme and alkaline ion have been widely investigated for commercial applications such as controlled-release devices and disposable plastics. Their degradation rate is strongly affected by structure, morphology, degradation medium, environmental condition etc. Among them, morphology plays a critical role in degradation phenomena because of controllable one by itself [1].

The solution-grown crystals (SGC) of polymers have been used as a model system for crystalline region [2]. l-PLA SGC were prepared by an isothermal crystallization from

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[*] Address correspondence to Won-Ki Lee, Dept. of Polymer Engineering, Pukyong National University, Busan 608-739, Korea. Tel.: (+82) 51-629-6451; Fax: (+82) 51-629-6429. E-mail: wonki@pknu.ac.kr

several diluted solutions and the obtained crystals had two kinds of morphologies, multistacked lozenge-shaped and hexagonal-shaped lamellar crystals [2, 3]. It has been reported that the alkaline hydrolysis of multistacked l-PLA SGC proceeded from both crystal edges and chain-folding surfaces because the molecular weights of the remained crystals and the lamella thickness were decreased [4]. In this study, we attempt to obtain further information on mechanism of alkaline hydrolysis of l-PLA SGC.

Experimental

l-PLA was synthesized by ring-open polymerization of l-LA in vacuum-sealed glass ampoules using stannous octoate. The l-PLA SGC were prepared by isothermal crystallization from 0.01% acetonitrile solution, collected by centrifugation, washed with methanol, then suspended in methanol. The details of are discussed elsewhere [5].

The pH for alkaline hydrolysis was controlled by adding NaOH. The samples for alkaline hydrolysis and elongation experiments were prepared by dropping crystal suspensions onto cleaned micas (5×5 mm^2) and PET films (50×10 mm^2), respectively. The crystals attached to the PET film were deformed by stretching of the PET films. The elongated film was glued onto a glass slide. Topographic images were obtained by a scanning force microscope, SPA 300 instrument with SPI 3700 controller (Seiko Instrument Co.) at room temperature. The cantilever was triangular with a microfabricated Si_3N_4 microtip. AFM images were carried out simultaneously 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.

Results and Discussion

To minimize any additional growth during the separation process at RT, the l-PLA SGC were grown from acetonitrile solution at 5°C below RT. Figures 1A and 1B show, typical electron micrograph and deflection pattern, respectively, of SGC with lozenge-shaped crystals which have unique dimensions of 12 μm of each side and ca. 11 nm thickness. The angles of growth faces are almost 60° and 120° with the orthogonal unit cell. The strong

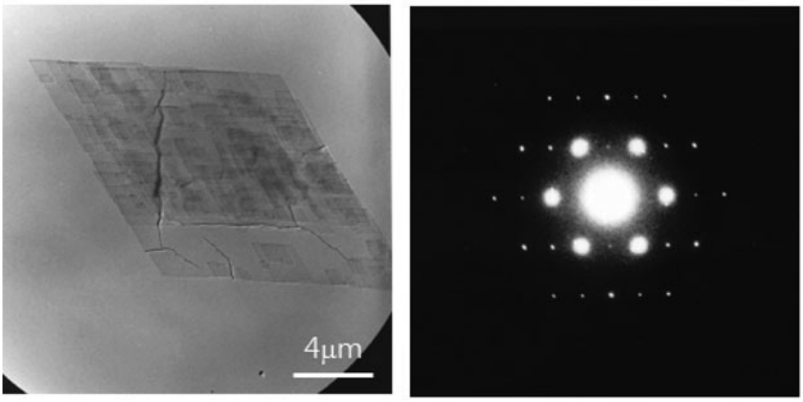

Figure 1. TEM image (left) and electron diffraction pattern (right) of l-PLA SGC.

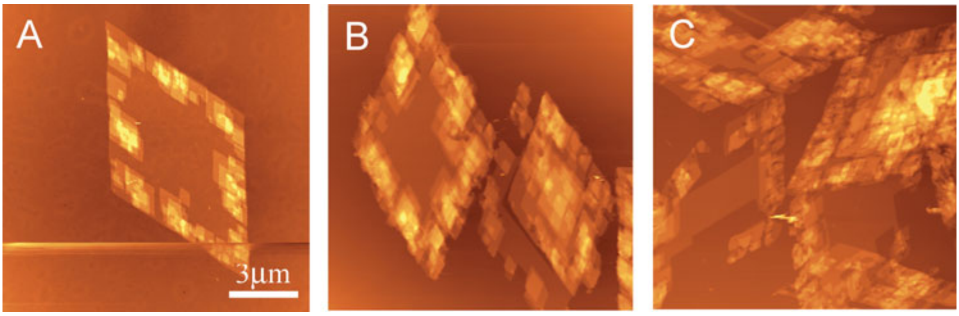

Figure 2. AFM topographic images of l-PLA SGC after alkaline hydrolysis at pH 10.7 of as-prepared (A), 30 min (B) and 150 min (C).

intensity of electron reflection indicates that molecular packing is very tight. A similar crystal morphology was observed when l-PLA attached substrate was grown [6].

Figure 2 shows atomic force microscopic images of l-PLA SGC after alkaline hydrolysis at 0.1 N NaOH. After 30 min, the lozenge-shaped erosion at the edges was observed in different sizes. Although the whole outline retains the original (lozenge-like) shape, small lozenge-shaped erosions at lateral sides and holes were observed after the increased hydrolysis time. Iwata and Doi [3] observed this kind of morphology after enzymatic degradation. Additionally, the enzymatic degradation showed the rounded morphology in l-PLA SGC. These different morphologies will be due to the molecular packing state. Since the alkaline ion as a degradation medium is much smaller than enzyme, ions are more susceptible to attack to relatively well packing chains than enzyme.

Our previous work [7] reported that the initial enzymatic degradation of PLA SGC by proteinase-K from the mold *Tritirachium album* occurred from the edges and in loose folding surfaces, resulting in unchanged molecular weight. Figure 3A shows molecular weight information before and after alkaline hydrolysis of l-PLA SGC. After the hydrolysis, new low molecular weight with narrow distribution (1.05) of ca. 6000 was observed. From the fiber repeating distance of 2.78 nm with 10/3 screw symmetry, it was reported that the molecular weight of remained chains after the hydrolysis which occurs in both chain-folding

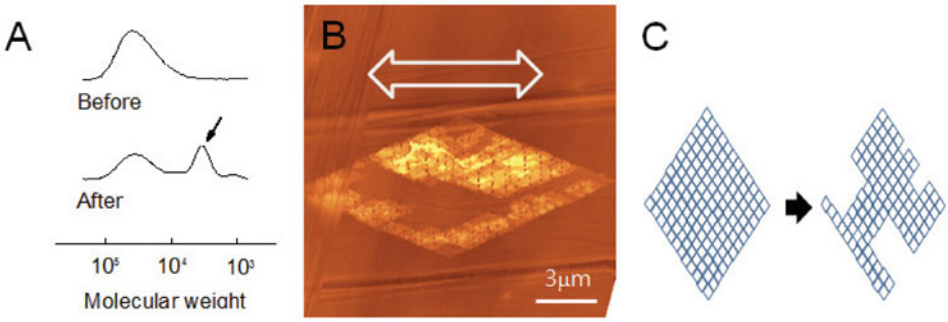

Figure 3. (A) Gel permeation chromatograms of l-PLA SGC before and after hydrolysis at 0.1 N NaOH for 100 min. The arrow indicates the fragment with low molecular weight. (B) AFM topographic image of l-PLA SGC after 10% elongation. The arrow indicates the elongation direction. (C) Schematic representation of alkaline hydrolysis of l-PLA SGC.

surface was 2,900 [2]. Our result is almost two times higher. It suggests that the hydrolysis of l-PLA SGC on mica occurs in one side of chain-folding surface. This is supported that the l-PLA SGC prepared in this study is in highly packing state. Figure 3B shows the AFM topographic images of the crystals after an elongation of ca.10%. Multiple cracks, which are almost perpendicular to the elongation direction, are found after the elongation. However, any morphological change parallel to the elongation direction (the compression) was not observed. This result indicates that the l-PLA SGC is in homogeneously packed state. Figure 3C shows the schematic representation for alkaline hydrolysis of l-PLA SGC. The l-PLA SGC were composed with a small size of lozenge-shaped unit with different packing states. Therefore, the hydrolysis by alkaline ions might occur in a relatively loosely packed unit where surrounding units are also affected in their packing states.

Conclusions

The alkaline hydrolysis of lozenge-shaped l-PLA SGC has been investigated by morphological observation after hydrolysis and deformation. From AFM images, the alkaline hydrolysis shows the lozenge-shaped erosion in the SGC. Also, the molecular weight After the hydrolysis, the fragment with low molecular weight was observed. This indicates that the initial hydrolysis of single crystals with alkaline ions occurred in loosely folding chains at the surface. A mechanical deformation of crystals by elongation of substrate leads to multiple cracks which are almost perpendicular to the elongation direction. These results suggest that a small size of lozenge-shaped unit is grown into the lozenge-shaped l-PLA SGC. Therefore, the hydrolytic behavior of l-PLA SGC is strongly related to the crystal growth.

Acknowledgments

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