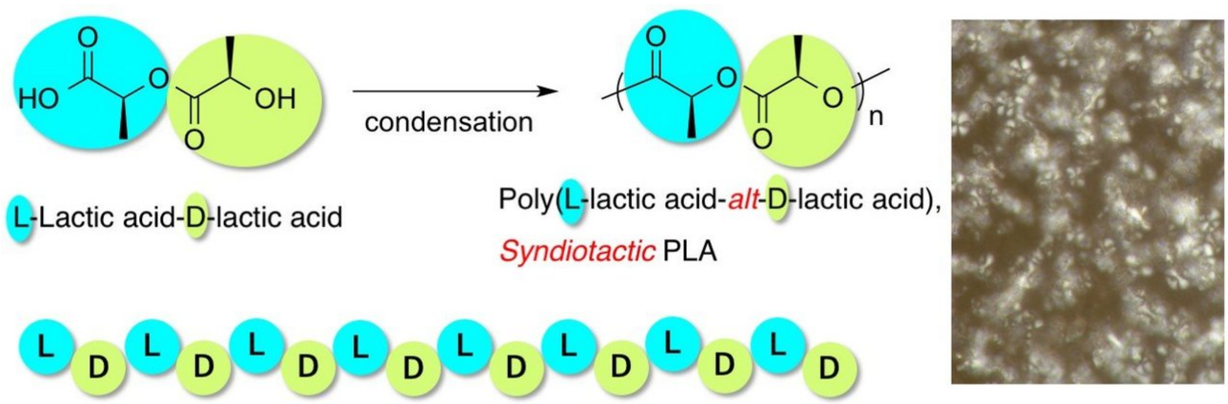
Method for synthesizing a novel polyester with alternating arrangement

May 11 2018



Method for synthesizing 'pure' syndiotactic poly(lactic acid) polyesters and picture of spherulite thereof. Graphical Abstract of *Polymer Chemistry*, 2018, 9, 2446-2457. DOI: 10.1039/C8PY00391B-Reproduced permission of The Royal Society of Chemistry. Credit: Toyohashi University of Technology. All Rights Reserved.

Professor Hideto Tsuji and Assistant Professor Yuki Arakawa at the Toyohashi University of Technology have developed a method for synthesizing a "pure" alternating copolymer of L- and D-lactic acids in which L- and D-lactic acids are alternately arranged, i.e., a syndiotactic poly(lactic acid). The results of the present study were published on April 10 in *Polymer Chemistry*, a journal published by the Royal Society of Chemistry (RSC). The results of this study make it possible to synthesize syndiotactic polyesters in which L- and D-type monomers are arranged alternately. These polyesters were traditionally considered to be difficult to synthesize. The present results are expected to facilitate the development of novel polyesters with unprecedented characteristics, such as good productivity due to a fast crystallization rate.

This research group conducts fundamental and applied research on bio-based polymers with a focus on "poly(lactic acid)s," which are polyesters that can be produced from reusable resources. One example of such a polylactide is starch derived from corn or potato. Poly(lactic acid)s are also typically known as "biodegradable polymers" and undergo hydrolysis in vivo, with the lactic acid in decomposition products being metabolized without adversely affecting the human body. These characteristics can be utilized for medical and environmental efforts, for example, for scaffolding materials in tissue regeneration.

Lactic acid is a monomer in poly(lactic acid)s and contains L- and D-type monomers, which have a symmetrical relationship, and poly(L-lactic acid) composed only of L-type lactic acid and poly(D-lactic acid) composed only of D-type lactic acid. These poly(lactic acid)s are also known as "isotactic" poly(lactic acid)s. Poly(lactic acid) also contains poly(DL-lactic acid), which possesses both L-lactic acid and D-lactic acid in equal quantities. Poly(DL-lactic acid) is mainly comprised of "atactic" poly(lactic acid) in which L- and D-type lactic acids are arranged randomly, and "syndiotactic" poly(lactic acid) in which L- and D-type lactic acids are arranged alternately. While it is simple to synthesize atactic poly(lactic acid), and syndiotactic poly(lactic acid) can be synthesized from meso-lactide (a cyclic ester composed of one molecule of L-lactic acid and one molecule of D-lactic acid) using a particular catalyst, synthesizing syndiotactic poly(lactic acid) with an arrangement purity of close to 100% has proven extremely difficult.

In the present study, the researchers have succeeded in synthesizing a dimer comprising one molecule of L-lactic acid and one molecule of D-lactic acid to synthesize a "pure" alternating copolymer with L- and D-lactic acids, i.e., a syndiotactic poly(lactic acid), by further increasing molecular weight through connecting those dimers to each other (FIG. 1). The alternating arrangement of L- and D-lactic acids in this synthesized syndiotactic poly(lactic acid) is approximately 100%, and wide-angle X-ray diffraction shows that the crystal structure thereof differs from poly(L-lactic acid) and poly(D-lactic acid) (with atactic poly(lactic acid) being amorphous). Syndiotactic poly(lactic acid) has been found to have excellent productivity due to having a higher crystallization rate than isotactic poly(lactic acid)s. In addition, although being a different type of polymer, syndiotactic polystyrene is known to differ from conventional polystyrene in terms of having high thermal resistance and high chemical resistance. As a result, the various characteristics of syndiotactic poly(lactic acid) are expected to greatly differ from those of isotactic poly(lactic acid)s and atactic poly(lactic acid).

The present disclosed method for synthesis can also be applied to polyesters derived from monomers of various optically active hydroxycarboxylic acids having a structure similar to that of lactic acid, to thereby synthesize a "pure" alternating copolymer of L- and D-type monomers, i.e., a syndiotactic polyester. A syndiotactic polyester synthesized using this method is expected to be a novel material different to isotactic and atactic polyesters that realizes unprecedented characteristics.

More information: Hideto Tsuji et al, Synthesis, properties, and crystallization of the alternating stereocopolymer poly(l-lactic acid-alt-d-lactic acid) [syndiotactic poly(lactic acid)] and its blend with isotactic poly(lactic acid), *Polymer Chemistry* (2018). DOI: 10.1039/C8PY00391B

Provided by Toyohashi University of Technology