

Control of Biodegradation of Polyesters by Molecular Design

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To utilize biodegradable polymers as a functional material, it is important to make the best use of their biodegradability. For improvement of reliability of biodegradation, control of biodegradation rate is indispensable, and conceivable approaches are 1) control of biodegradation by molecular design, and 2) numerical analysis of environmental parameters concerned with biodegradation. In this paper, the former study is described and the latter is explained in the other paper.

We have systematically synthesized various polymers, and studied their biodegradation as being related to their molecular structures. Biodegradation was mainly evaluated by enzymatic hydrolysis with lipases. Hydrolysis was influenced by copolymer composition, lengths of methylene chain in the backbone, and substituents. In the case of copolymers, the polymer composition is a rather important factor, and the biodegradability showed the maximum at a certain composition depending on the ester content, the randomness, and crystallinity. The methyl group suppresses the degradation strongly. The copolymers having long methylene chains ($n=3-5$) in repeating unit showed high biodegradability and it can be explained with flexibility of the polymer chain. Poly(glycolic acid) is equivalent to $n=1$ (methylene chain), and this type of structure showed exceptional results, that is high hydrolyzability. Aromatic groups and unsaturated groups, as a side chain or in main chain, had an inhibitory effect on biodegradation. Hydrophilicity promotes biodegradability. The difference of molecular weights did not show effects clearly. This tendency is based on enzymatic hydrolyzability, and approximately agreed with that by an activated sludge test. Control of biodegradation by molecular design is available with the knowledge.

Poly(L-lactic acid) is a famous bio-based and biodegradable polymer, though its application is limited because it is a brittle material and its biodegradation in environment is rather slow. In order to control biodegradation of poly(L-lactic acid), copolymerization with lactones is a promising and convenient method. That is, even 10% of lactone contents resulted in drastic acceleration of biodegradation and a maximum was at 20-30% of lactone contents in enzymatic hydrolysis test. On the contrary, a maximum by a activated sludge test is around 70-80% of lactone content, for example ϵ -caprolactone. This difference should be explained as balance between intrinsic high hydrolyzability and crystallinity of poly(L-lactic acid) homopolymer and enzymatic biodegradability of polylactones (polyesters). Polymer modification using the molecular design mentioned above would be key ingredient in wide and rapid diffusion of utilization of biodegradable polymeric

materials.