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Tailoring the Interplay between Two Monomers in the Properties of Degradable Polyesters Synthesized via Ring-Opening Alternating Copolymerization

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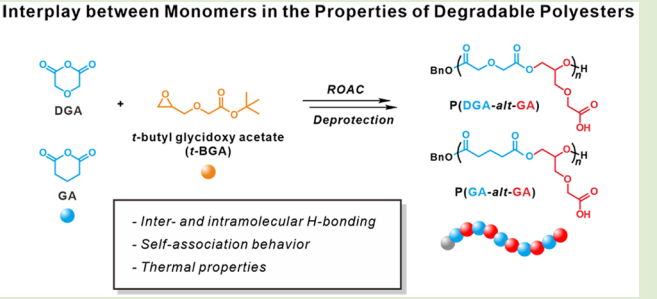
ABSTRACT: Ring-opening alternating copolymerization (ROAC) of cyclic anhydrides and epoxides has emerged as a powerful strategy to produce degradable polyesters with a diverse array of structures from the combination of two distinct building blocks. In this work, we exploited the organocatalytic ROAC of cyclic anhydrides and a functional epoxide, *t*-butyl glycidoxy acetate, followed by acidic deprotection to access degradable polyesters with carboxylic acid pendants. To study the interplay between monomers, diglycolic anhydride and glutaric anhydride were used as cyclic anhydrides to prepare two polyesters. In particular, the effects of the oxygen heteroatom in the cyclic anhydrides on the properties of the carboxylic acid-containing polyesters were investigated. The introduction of the oxygen heteroatom into the cyclic anhydrides significantly influenced their thermal properties and pH-dependent self-association behavior in an aqueous solution. Furthermore, molecular dynamics simulations elucidate that the number and type of hydrogen bonds play a crucial role in the self-association behavior between the polymers both in the solution and bulk states. The findings of this study highlight the importance of the interplay between monomers in the design of functional polyesters with tunable properties.



The continuously increasing environmental pollution caused by nondegradable petroleum-based plastics has become a global issue.[1] Recently, degradable polymers have emerged as suitable alternatives to nondegradable plastics owing to their advantageous properties, especially their ability to degrade at a faster rate without causing significant environmental concerns. Aliphatic polyesters are sustainable alternatives because of their numerous renewable sources, facile hydrolytic degradation, and high biocompatibility.[2] Consequently, they are widely used in packaging, tissue engineering, and biomedical devices.[3−5]

Among the well-known synthetic routes to polyesters, the step-growth approach has reached maturity; however, it typically requires harsh conditions and the removal of byproducts. Ring-opening polymerization (ROP) of lactones has also been studied extensively, although the resulting polyesters have a limited range of properties, owing to the minimal functional diversity of the available lactones. An alternative chain-growth route to polyesters is the ring-opening alternating copolymerization (ROAC) of cyclic anhydrides and epoxides.[6−8] The combinations of two distinct monomers enable the production of degradable polyesters with a diverse array of structures.

One appealing aspect of the ROAC of cyclic anhydrides and epoxides is the use of two types of monomers, which facilitate the synthesis of polymers with wide structural diversity. To date, several commercially available monomers, such as propylene oxide, cyclohexene oxide, and phthalic anhydride, have been widely studied. Interestingly, further advancements have made it possible to explore more functionally diverse monomers for achieving polyesters with specific functionalities. As a representative example, Coates and co-workers synthesized renewable tricyclic anhydrides and copolymerized them with propylene oxide and cyclohexene oxide to tune the glass-transition temperature (T_g) of the polymers and enhance their sustainability.[9] Moreover, the ROAC of a D-xylose-based oxetane with cyclic anhydrides was demonstrated to synthesize an array of sugar-based polyesters, which were amenable to further postpolymerization functionalization through the hydroxyl group and internal alkene.[10] The recent study of copolymerization of fatty acid-based epoxides and various cyclic anhydrides afforded functional polyesters, which can form rigid macromolecular networks upon subsequent cross-linking processes.[11] However, systematic studies used to investigate the influence of the interplay between two

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