Bio-based polymer design based on oligosaccharide

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Polysaccharides and their derivatives have long been utilized as thermoplastics and fibers. However, despite the long history of utilizing polysaccharides in commodity polymers, their range of applications has been limited due to their intrinsically hard and rigid properties. Here, we report that the integration of a rubbery hydrophobic polymer and oligo/polysaccharide hard segments into a block copolymer (BCP) can create a novel bio-based elastomer, in which the microphase-separated carbohydrate hard domains act as a physical cross-link for the rubbery chains.

A series of "hard-*b*-soft-*b*-hard" BCPs consisting of maltooligosaccharides (maltose, maltotriose, maltotetraose, and maltohexaose; A block) and poly(δ-decanolactone) (PDL; B block), with ABA-, A_2BA_2-, A_3BA_3-, $A(BA)_2$-, and $A_2(BA)_2$-type architectures, were synthesized by combining living ring-opening polymerization and Cu-catalyzed azido-alkyne click reaction.[1] To understand the correlation between the BCP molecular structure and material properties, the BCPs were designed to have comparable molecular weights (around 12 kg mol^{-1}) and total numbers of glucose units (12 units). Morphological analysis revealed the formation of well-ordered body-centered-cubic sphere and hexagonally close-packed cylinder (HEX) morphologies depending on the branched architecture (interdomain distance 9.7−14.4 nm). While the PDL homopolymer is a viscous liquid due to its low T_g and amorphous nature, all BCPs exhibited elastomeric properties, confirming that the oligosaccharide blocks acted as the hard domains to cross-link the rubbery PDL chains. Tensile testing revealed that the mechanical properties of the BCPs were mainly determined by the microphase-separated structure and less affected by the length of each oligosaccharide chain. The HEX-forming A_2BA_2- and A_3BA_3-type BCPs exhibited Young's moduli of ~6 MPa, which is comparable to well-known styrene-based thermoplastic elastomers.

To avoid possible competition with food supply, we are recently trying to replace the amylose-derived maltooligosaccharide block by inedible cellulose-derived oligosaccharides. By applying the above-established molecular design, we have designed and synthesized the ABA-type triblock copolymers with acetyl celloologosaccharide blocks.[2,3] Interestingly, the acetyl cellooligosaccharide-based BCPs outperformed its maltooligosaccharide counterparts in the mechanical properties.

These results demonstrate that oligosaccharides are a sustainable alternative to the petroleum-derived synthetic hard segments (e.g., polystyrene).

1) Isono, T. et al., *Macromolecules* **2020**, 53, 5408. 2) Katsuhara, S. et al., *ACS Sustainable Chem. Eng.* **2021**, *9*, 9779. 3) Katsuhara, S. et al., *Carbohydr. Polym.* **2023**, *316*, 120976.