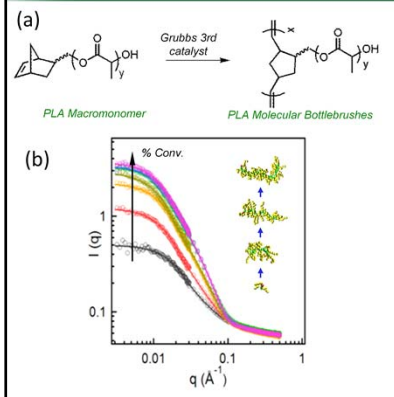
Structural Evolution of Poly(lactide) Molecular Bottlebrushes



(a) Reaction scheme for PLA molecular bottlebrushes. (b) SANS curves of PLA molecular bottlebrushes collected at different polymerization times. Images show configurations of the molecular bottlebrushes during polymerization captured by CG-MD.

Work performed at the Center for Nanophase Materials Sciences, the Spallation Neutron Source, the HANARO center (Republic of Korea), and the University of Tennessee.

Scientific Achievement

The structural evolution of poly(lactide) (PLA) molecular bottlebrushes was revealed during the process of polymerization.

Significance and Impact

The understanding gained from the polymerization of molecular bottlebrushes is applicable to other architecturally complex polymers, thereby enabling the design of new multifunctional soft matter materials.

Research Details

- Size exclusion chromatography and small-angle neutron scattering (SANS) were performed for various reaction times during polymerization.
- SANS data were fit using the flexible cylinder model considering internal density fluctuation.
- Bottlebrush architecture and reaction kinetics were modeled using coarse-grained molecular dynamics (CG-MD).

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Narrative Highlight Text:
Understanding the polymerization kinetics plays a central role in identifying the underlying polymerization mechanism which is critical to facilitate development of complex multifunctional soft matter materials. In this work, the structural evolution from poly(lactide) (PLA) macromonomer to the resultant PLA molecular bottlebrush during ring opening metathesis polymerization (ROMP) was investigated for the first time by combining size exclusion chromatography (SEC), small-angle neutron scattering (SANS), and coarse-grained molecular dynamics (CG-MD) simulations. Multiple aliquots were collected at various reaction times during ROMP and subsequently analyzed by SEC and SANS. These complementary techniques enable the unique understanding of changes in conversion, molecular weight and polydispersity as well as structural details of PLA molecular bottlebrushes. We find that PLA molecular bottlebrushes undergo three conformational transitions with increasing conversion (i.e., increasing the backbone length): (1) from an elongated to a globular shape due to longer side chain at low conversion, (2) from a globular to an elongated shape at intermediate conversion caused by excluded volume of PLA side chain, and (3) the saturation of contour length at high conversion due to chain transfer reactions.

Reference
"Structural Evolution of Polylactide Molecular Bottlebrushes: Kinetics Study by Size Exclusion Chromatography, Small Angle Neutron Scattering, and Simulations"
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