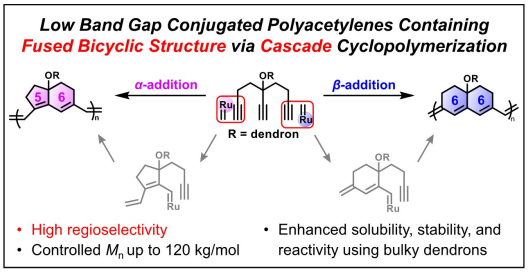
Cascade Cyclopolymerization of 5-Ethynyl-1,8-Nonadiyne Derivatives to Synthesize Low Band Gap Conjugated Polyacetylenes Containing a Fused Bicyclic Structure

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Cyclopolymerization is a powerful method for synthesizing polyacetylenes containing four- to seven-membered rings. However, the structure of the repeat unit only consists of mono-cycloalkene due to the single cyclization of diyne monomers. Herein, we demonstrate a novel cascade cyclopolymerization to synthesize polyacetylenes containing fused bicyclic rings from triyne monomers containing bulky dendrons via sequential cascade ring-closing metathesis. These dendrons provided solubility and stability to the rigid bicyclic polyacetylene backbone. In addition, we controlled the regioselectivity of the catalyst approach by altering its structure and synthesized polymers containing fused bicyclo[4,3,0] or [4,4,0] rings with high molecular weights of up to 120 kg/mol. Interestingly, the resulting polymers showed narrower band gaps (down to 1.6 eV) than polymers with mono-cycloalkene repeat units due to the planarization of the conjugated segment resulting from the fused bicyclic structure.



[1] Hanseul Ryu, Jong-Chan Sung, Gangme Kim, Yan Xu, Robert H. Grubbs, Tae-Lim Choi*, *Angew. Chem. Int. Ed.* **2022**, 61, e202210244.