

Polymerization of Arynes Initiated by a Nitrogen Nucleophile

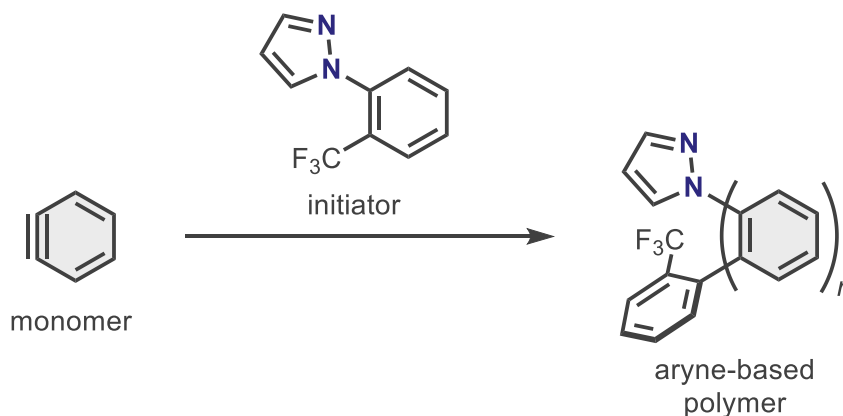
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Arynes are attractive monomers for the direct incorporation of *o*-arylene units into polymer backbones, but their extremely high reactivity and short lifetimes have limited their use in polymer synthesis.[1-3] We have studied nitrogen-nucleophile-initiated aryne polymerization as a strategy to address this challenge. First, we found that *N*-aryl pyrazoles initiate nucleophilic aryne polymerization to give poly(*ortho*-arylene)s, providing a direct synthetic route to sterically congested *o*-arylene-based polymers.[4] The polymerization proceeds via a Truce–Smiles rearrangement pathway, and the persistent pyrazole active site suppresses undesired chain termination and chain transfer. We then extended this concept to copolymerization and achieved alternating copolymerization of arynes with carbonyl compounds by using nitrogen nucleophiles as initiators. This method enables direct construction of polymers containing both *o*-arylene units and carbonyl-derived linkages from highly reactive aryne monomers. These results demonstrate that nitrogen-nucleophile initiation offers a versatile platform for aryne-based polymerization, enabling both homopolymerization and alternating copolymerization. This study expands the scope of aryne polymerization and provides a new strategy for the synthesis of structurally unique aromatic polymers.



References 1) E. Ihara, A. Kurokawa, T. Koda, T. Muraki, T. Itoh, K. Inoue, *Macromolecules* 38, 2167-2172 (2005). 2) S. Ito, K. Takahashi, K. Nozaki, *J. Am. Chem. Soc.* 136, 7547-7550 (2014). 3) Y. Mizukoshi, K. Mikami, M. Uchiyama, *J. Am. Chem. Soc.* 137, 74-77 (2015). 4) H. Fujimoto, S. Yamamura, M. Tobisu, *J. Am. Chem. Soc.* 147, 22302-22308 (2025).

Biography (For Plenary, Keynote, and Invited Speakers)

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Personal History:

Hayato Fujimoto received his B.Sc. degree from The University of Osaka under the supervision of Prof. Toshiyuki Moriuchi and Prof. Toru Amaya (2017). He obtained his M.Sc. (2019) and Ph.D. (2022) degrees from the same university under the supervision of Prof. Mamoru Tobisu. In 2022, he joined Prof. Tobisu's group as an assistant professor at The University of Osaka. His research interests focus on the development of new polymerization and synthetic methods.

Research Keyword

Polymerization, Aryne, Catalyst, Atomic Carbon