



Aryne polymerization by organonucleophile

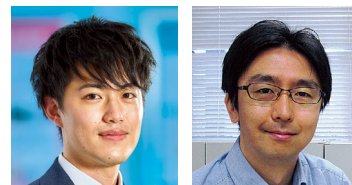
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Abstract

Arynes which results from the abstraction of two neighboring hydrogen atoms of an aromatic ring, plays key roles in modern organic synthesis. However, aryne polymerization, in which arynes act as monomers to form polymer chains, has long been considered challenging due to their inherent instability. In this study, we discovered that a simple organonucleophile, *N*-arylpyrazole, can serve as an effective initiator to promote aryne polymerization without the need for transition-metal catalysts. The reaction proceeds through a unique mechanism that combines nucleophilic addition and intramolecular aromatic substitution (S_NAr), allowing the controlled formation of poly(*ortho*-arylene) structures with narrow molecular weight distributions.

Background & Results

Aromatic polymers exhibit excellent electrical and mechanical properties and have been widely used as functional materials in electronics and energy devices. Among them, poly(*ortho*-arylene)s are particularly attractive because of their helical π -conjugated structures, which give rise to distinctive optical and electronic properties. Nevertheless, their synthesis has remained difficult, and controlled polymerization using arynes as monomers had not been achieved due to uncontrolled side reactions and premature chain termination.

To overcome this limitation, we focused on *N*-arylpyrazole as a neutral organonucleophilic initiator. The pyrazole ring exhibits both nucleophilicity and chemical robustness, enabling nucleophilic addition to the aryne followed by an intramolecular S_NAr reaction. This process proceeds through a pyrazole-induced Truce–Smiles rearrangement, in which the *N*-aryl bond is successively inserted by the aryne, while regenerating the pyrazole unit at the growing chain end. As a result, the polymerization can proceed in a controlled chain-growth manner.

Experimentally, MALDI-TOF mass spectrometry confirmed that the repeating units were regularly connected, and the obtained polymers exhibited narrow dispersity. Moreover, the robustness of the pyrazole motif allowed us to extend this approach to graft-type and star-shaped polymers. These findings clearly demonstrate that aryne polymerization can be precisely controlled through rational organic molecular design, without the assistance of metal catalysts.

Significance of the research and Future perspective

This study establishes a new concept of neutral nucleophile-driven polymerization, representing the first example of aryne

polymerization using organonucleophiles. The unique reactivity of the pyrazole unit enables stable propagation and suppresses undesired side reactions, opening a new avenue for the synthesis of structurally defined aromatic polymers. Beyond aryne systems, this strategy provides a versatile framework for the development of next-generation π -conjugated materials, conductive polymers, and optically active molecular architectures. Moving forward, we aim to expand this methodology to other reactive monomer classes and explore its potential in creating functional polymeric materials with tailored electronic and optical properties.

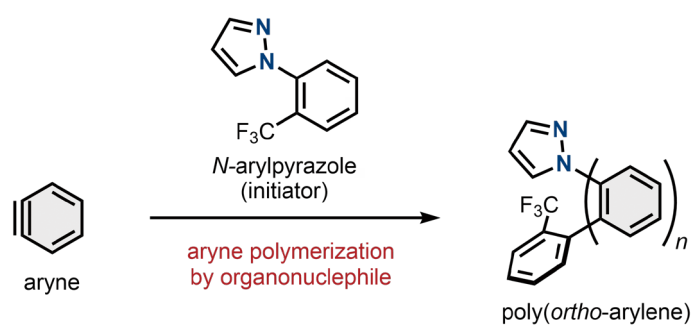


Figure 1.

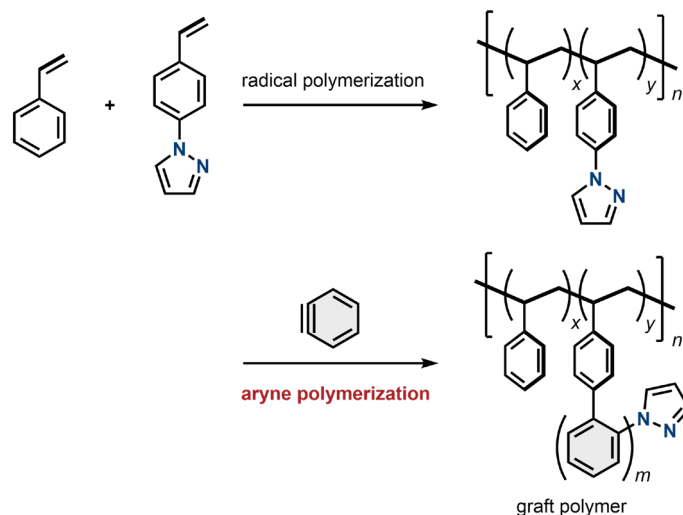


Figure 2.

Patent

Treatise

Fujimoto, Hayato; Yamamura, Shisato; Tobisu, Mamoru. Aryne polymerization enabled by pyrazole-induced nucleophilic aromatic substitution. *J. Am. Chem. Soc.* 2025, 147(26), 22302–22308. doi: 10.1021/jacs.5c03980
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URL

<https://www-chem.eng.osaka-u.ac.jp/~tobisu-lab/English.html>

Keyword

organic synthesis, polymer, aryne