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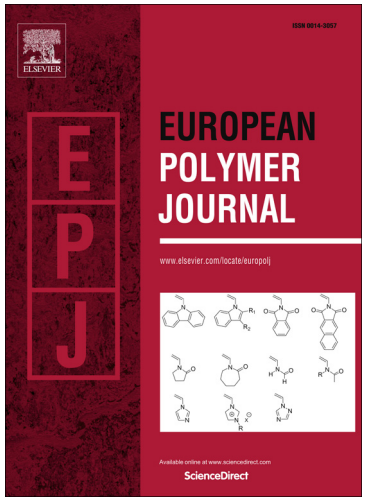

Flash Cationic Polymerization Followed by Bis-end-functionalization. A New Approach to Linear-Dendritic Hybrid Polymers

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Flash Cationic Polymerization Followed by Bis-end-functionalization. A New Approach to Linear-Dendritic Hybrid Polymers

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Abstract

Cationic polymerization of vinyl ethers using a multifunctional dendritic initiator and multifunctional terminators in a flow microreactor system gave polymers having multiple functionalities on both ends. Subsequent transformation of the resulting polymers through Suzuki-Miyaura coupling and/or copper-mediated azide-alkyne cycloaddition gave linear-dendritic hybrid polymers.

Keywords*: Flow microreactor, Cationic polymerization, Dendritic cation pool, Functionalized linear-dendritic hybrid polymer, Cross-coupling reaction*

Introduction

Linear-dendritic (L-D) polymers are intriguing and promising macromolecules in materials science,[1] and the ambivalent character of their architecture offer unique possibilities for numerous emerging applications.[2] There are, in principle, three strategies to synthesize L-D polymers (Figure 1):[1c] (a) dendron-first strategy:[3] the synthesis of a dendrimer followed by polymerization initiated at the dendrimer, (b) coupling strategy:[4] coupling of a dendrimer and a functional linear polymer chain, and (c) chain-first strategy:[5] the synthesis of a terminally functionalized polymer chain and the subsequent construction of a dendrimer.

Previously, we reported a dendron-first approach to linear-dendritic polymers through cationic polymerizations of vinyl ethers initiated by dendritic diarylcarbenium ion **2**, which was generated by anodic oxidation of corresponding organosilane **1** at –78 °C (Scheme 1).[6] Using flow microreactors[7–9] featured by fast mixing, fast heat transfer and precise residence time control, the cationic polymerizations proceeded in a "living" manner.[10,11] Thus, polymers having narrow molecular weight distribution were obtained, and living polymer end could be used for block co-polymerization. Importantly, the living polymer end could also be terminated efficiently with a silyl enol ether and allyltrimethylsilane. In addition, the reaction tolerates aryl bromide moieties derived from **2**.

We envisioned that by using a properly functionalized terminator in this flash[12] cationic polymerization, polymers with

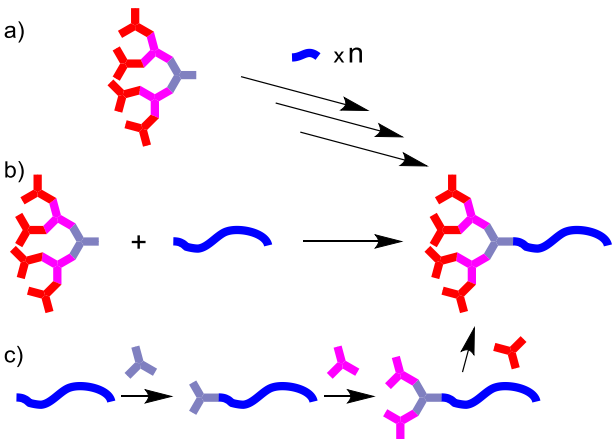
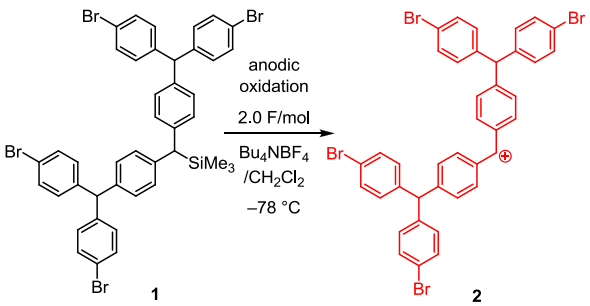


Figure 1. Synthetic strategies for linear-dendritic polymers; (a) dendron-first strategy, (b) coupling strategy, (c) chain-first strategy.



Scheme 1. Electrochemical generation of diarylcarbenium cation **2**.

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