



Polymerization of vinyl ethers initiated by dendritic cations using flow microreactors



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ABSTRACT

Cationic polymerization of vinyl ethers initiated by an electrogenerated dendritic diarylcarbenium ion in the presence of 2,6-di-*tert*-butylpyridine was developed using a flow microreactor. The carbocationic polymer end generated by polymerization of isobutyl vinyl ether was effectively trapped by various nucleophiles such as trimethyl(1-phenylvinyl)oxy)silane and allyltrimethylsilane to give polymers with very narrow molecular weight distribution. The block copolymerization of two vinyl ethers followed by trapping with nucleophiles was successfully accomplished to give structurally well-defined macromolecules.

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1. Introduction

Linear-dendritic polymers have emerged as a new important type of macromolecules in materials science,¹ and the ambivalent characteristics of their architecture offer unique/new possibilities for numerous potential applications.² Linear-dendritic polymers can be prepared based on three strategies:^{1c} (1) coupling strategy:³ coupling of a dendrimer and a functional linear polymer chain, (2) chain-first strategy:⁴ the synthesis of a terminally functional polymer chain and the subsequent construction of a dendrimer, and (3) dendron-first strategy:⁵ the synthesis of a dendrimer followed by polymerization initiated at the dendrimer. Especially the dendron-first approach is very useful because the dendrimers can be constructed by a convergent synthetic route such as coupling of prefabricated branched units.

We have developed the cation pool method in which organic cations are electrochemically⁶ generated and accumulated in solution in the absence of nucleophiles and are used for the reactions with subsequently added nucleophiles.⁷ The method has been successfully applied to various organic cations including *N*-acyliminium ions, alkoxy-carbenium ions, and diarylcarbenium ions. We have also developed an iterative process for making dendritic structures based on the cation pool method; a sequence consisting of the electrochemical generation of a diarylcarbenium ion (activation) followed by the reaction with (diphenylmethyl)

trimethylsilane as a building block (coupling) is repeated to effect convergent synthesis of dendritic molecules (Fig. 1).⁸ Notably, dendritic diarylcarbenium ions react with unfunctionalized polystyrenes to give dendronized polymers.⁹

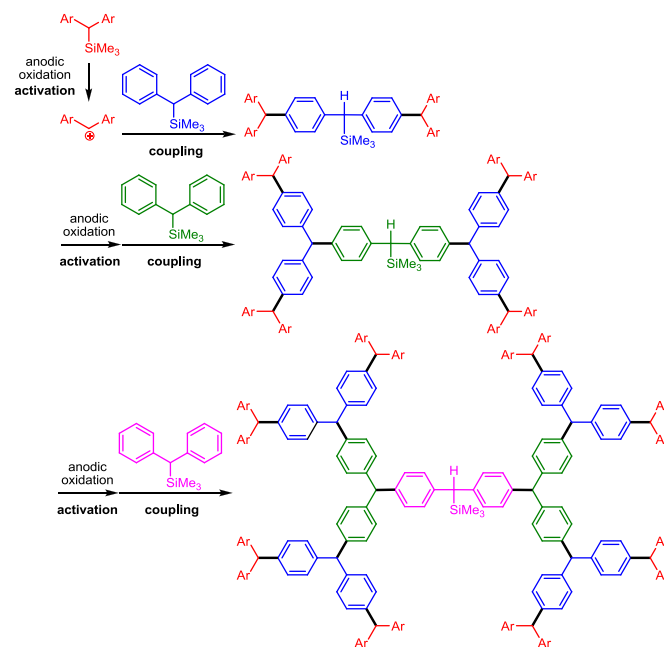


Fig. 1. An iterative process for making dendritic structures based on the cation pool method.

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Chemical synthesis in flow microreactors^{10,11,12} has attracted a great deal of attention and the applications to polymerization of vinyl monomers have been extensively studied.¹³ For example, controlled cationic polymerization^{14,15} of vinyl ethers and controlled anionic polymerization^{16,17} of styrenes, alkyl methacrylates, and *tert*-butyl acrylate using flow microreactors have been reported in the literature. The molecular weight and the molecular weight distribution can be strictly controlled by virtue of the characteristic features of flow microreactors such as fast mixing, fast heat transfer, and precise residence time control.

Based on these achievements, the following working hypothesis came to our mind. Use of dendritic diarylcarbenium ions as initiators of controlled cationic polymerization in flow microreactors leads to the formation of linear-dendritic polymers bearing living polymer ends, which can be trapped with nucleophiles (dendron-first strategy). The method would serve as a powerful and straightforward way of synthesizing structurally well-defined linear-dendritic polymers. However, to the best of our knowledge, such an approach has not yet been reported so far, although studies using ring-opening polymerizations^{5c} and living radical polymerizations^{5c–e} have been reported. The concept works, and we report herein the results of this proof-of-principle study.

2. Results and discussion

2.1. Cationic polymerization of isobutyl vinyl ether initiated by a dendritic diarylcarbenium ion pool

We chose to study diarylcarbenium ion **2**¹⁸ as a model of a dendritic initiator of the cationic polymerization. Cation **2** was generated by low temperature electrochemical oxidation of **1**, which has a silyl group as an electroauxiliary¹⁹ for the selective oxidation and peripheral bromo functionalities for future functionalization (Fig. 2).

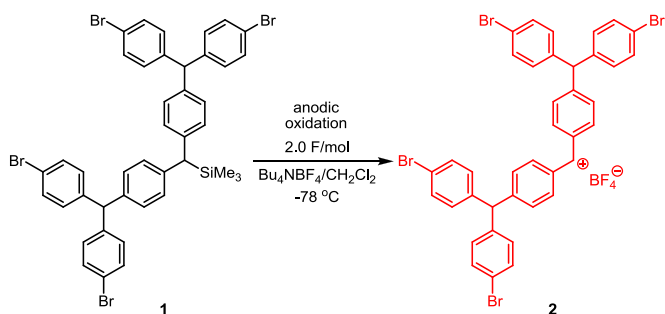


Fig. 2. Generation of diarylcarbenium ion **2**.

First, we examined the polymerization of isobutyl vinyl ether using diarylcarbenium ion **2** in a flow microreactor system composed of two T-shaped micromixers (**M1** and **M2**) and two microtube reactors (**R1** and **R2**) (Fig. 3). The flow microreactor system was dipped in a cooling bath ($-78\text{ }^{\circ}\text{C}$). A solution of isobutyl vinyl ether (0.50 M in CH_2Cl_2 , 10 mL/min) and a solution of **2** (0.050 M in CH_2Cl_2 , 5 mL/min) were mixed using **M1** ($\phi=250\text{ }\mu\text{m}$). The mixed solution was introduced to **R1** ($\phi=1000\text{ }\mu\text{m}$, $L=25\text{ cm}$), where the polymerization took place. The polymerization was terminated by adding a solution of trimethyl(1-phenylvinyl)oxysilane (1.0 M in CH_2Cl_2 , 5 mL/min) at **M2** ($\phi=500\text{ }\mu\text{m}$) and **R2** ($\phi=1000\text{ }\mu\text{m}$, $L=50\text{ cm}$) to obtain the end-functionalized polymer **3**. When the polymerization was carried out in the presence of a proton trapping agent, the agent was added to a solution of **2** prior to the polymerization.

Fig. 4 shows MALDI-TOF mass spectra of the resulting polymers. The polymer produced in the absence of a proton trapping agent is

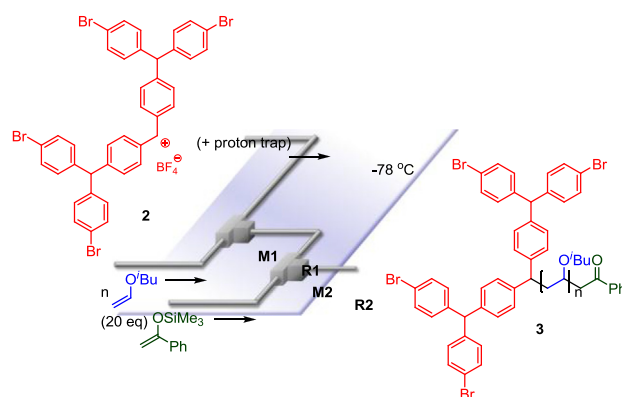


Fig. 3. Flow microreactor for cationic polymerization of isobutyl vinyl ether initiated by diarylcarbenium ion **2** in the absence or presence of a proton trapping agent at $-78\text{ }^{\circ}\text{C}$. T-shaped micromixers: **M1** and **M2**. Microtube reactors: **R1** and **R2**.

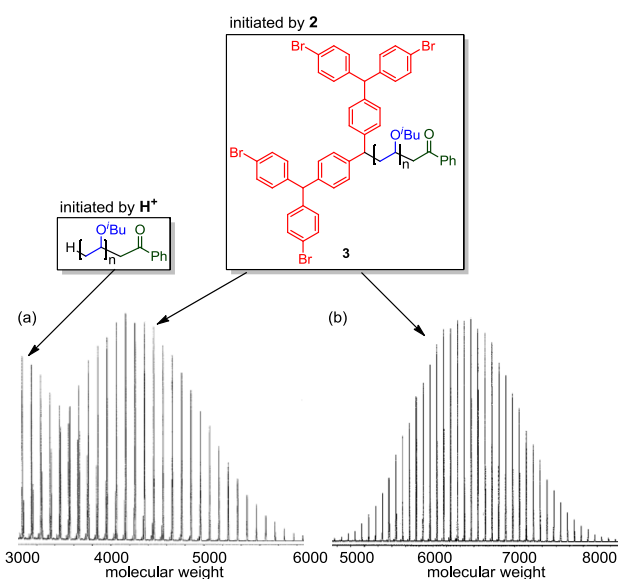


Fig. 4. MALDI-TOF mass spectra of the polymers obtained by (a) the polymerization in the absence of a proton trapping agent and (b) the polymerization in the presence of 2,6-di-*tert*-butylpyridine (0.5 equiv).

contaminated with a significant amount of the polymer obtained by proton-initiated polymerization (Fig. 4a).

Polymerizations in the presence of 1,8-bis(dimethylamino)naphthalene as a proton trapping agent resulted in much low yields of polymer **3**, although **3** was obtained in good yields in the absence of a proton trapping agent (Table 1). In contrast, polymerizations using 2,6-di-*tert*-butylpyridine as a proton trapping agent gave **3** in good yields.

Table 1
Cationic polymerization of isobutyl vinyl ether initiated by diarylcarbenium ion **2** in the absence or presence of a proton trapping agent using a flow microreactor system

Proton tapping agent		Mn ^a	Mw/Mn ^a	Yield (%)
	—	5200	1.08	Quant
	0.3 equiv	13,400	1.10	61
	0.5 equiv	12,100	1.19	22
	1.0 equiv	16,100	1.11	6
	0.3 equiv	6600	1.06	87
	0.5 equiv	8100	1.05	83
	1.0 equiv	9000	1.05	90

^a Polymers were analyzed with size-exclusion chromatography calibrated with polystyrene.

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