



Suzuki polycondensation and post-polymerization modification toward electro-optic perfluorocyclobutyl (PFCB) aryl ether polymers: Synthesis and characterization

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ABSTRACT

Suzuki polycondensation (SPC) as an alternative strategy has been utilized for the first time to readily yield functional perfluorocyclobutyl (PFCB) aryl ether polymers, which are difficult to obtain via the traditional [2+2] thermal cyclopolymerization strategy. Using two reactive PFCB aryl ether molecules as monomers, the biphenyl PFCB aryl ether polymer without any functionality was first prepared and exhibited good thermal stability, up to 450 °C at 8% weight loss (N₂). By choosing appropriate functional monomers, aldehyde-functionalized PFCB aryl ether polymer precursor was also successfully prepared. Post-polymerization modification of this polymer precursor via Knoevenagel condensation yielded three distinct PFCB aryl ether polymers containing thermally stable triarylamine-based electro-optic chromophores.

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1. Introduction

Perfluorocyclobutyl (PFCB) aryl ether polymers are a unique class of amorphous semi-fluorinated polymers, which exhibit a combination of high performance properties such as excellent thermal stability, oxidative stability, chemical resistance, low surface energy, low optical loss, and high electrical insulating ability [1]. As a result, PFCB aryl ether polymers have been utilized in many areas, such as proton exchange membranes (PEMs) in hydrogen–oxygen fuel cells [2], organic nonlinear optic (NLO) host polymers [3–6], organic nanomaterials [7], photonics [8], fire retardant materials, and polymer light emitting diodes [9,10].

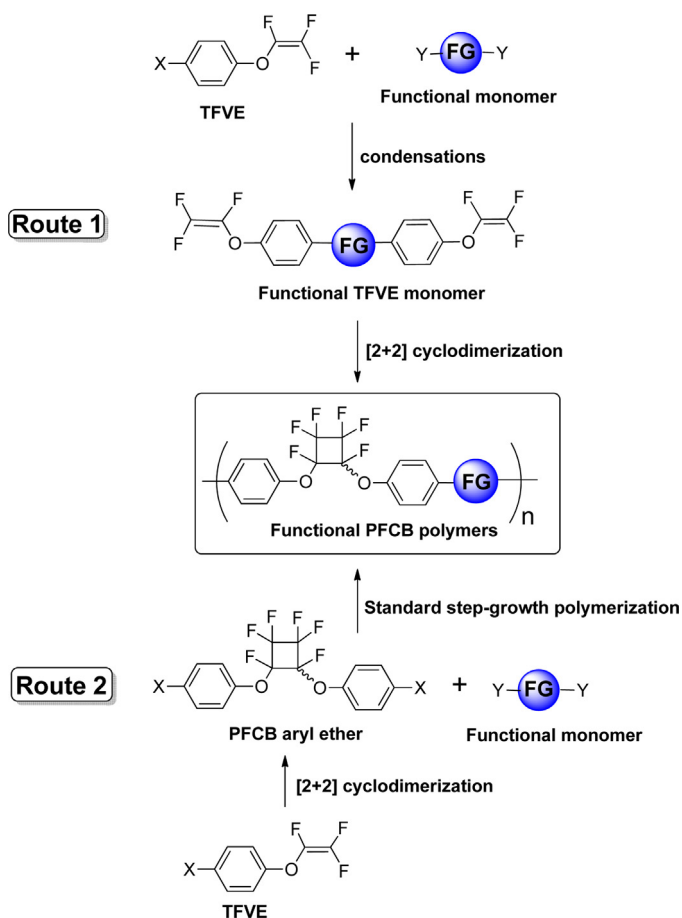
Introduction of functionalities into PFCB aryl ether polymers is used to tailor their applications. Functional PFCB aryl ether polymers are traditionally prepared via a [2+2] thermal cyclodimerization of appropriate functional aromatic trifluorovinylether (TFVE) monomers above 150 °C in bulk or in a solution without any catalyst (Scheme 1, Route 1) [11]. Functional TFVE monomers usually are prepared via reactions of their corresponding functional monomer precursors with the mono-functional reactive

TFVE molecules (e.g. p-trifluorovinyl bromobenzene or p-trifluorovinyl benzoic acid, Scheme 1, Route 1). This attractive technology has some limitations. When complex functional structures are required, sometimes it is difficult or impossible to synthesize the corresponding functional TFVE monomers. Direct polymerization of functional TFVE monomers via the [2+2] thermal cyclodimerization cannot always yield desired functional PFCB aryl ether polymers because some functional groups cannot tolerate the high polymerization temperature or may undergo side reactions with TFVE groups during the polymerization process. It has been observed that hydrocarbon olefins (e.g. the double bonds in conjugated NLO chromophores) and aldehyde groups can undergo thermal [2+2] cycloaddition reaction with TFVE groups [12,13].

Alternatively, functional PFCB aryl ether polymers can be prepared via the standard step-growth polymerization of reactive PFCB aryl ether monomers with functional monomers (Scheme 1, Route 2). Reactive PFCB aryl ether monomers are usually prepared from their corresponding mono-functional TFVE molecules via the thermal [2+2] cyclodimerization (Scheme 1, Route 2) [12,14–18]. The synthetic Route 2 has some obvious advantages: functional monomers are much easier to synthesize compared to their corresponding functional TFVE monomers and polymerizations can be performed at much lower temperatures. Up to now, Wittig condensation polymerization [12], the Huisgen's 1,3-dipolar

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Scheme 1. Two synthetic routes to synthesize functional PFCB aryl ether polymers.

cycloaddition polymerization [19], nucleophilic aromatic substitution polymerization [18], and palladium catalyzed amination polymerization [15] have been successfully performed to prepare functional PFCB aryl ether polymers via the synthetic Route 2. To our best knowledge, Suzuki polycondensation has not been utilized to prepare functional PFCB aryl ether polymers.

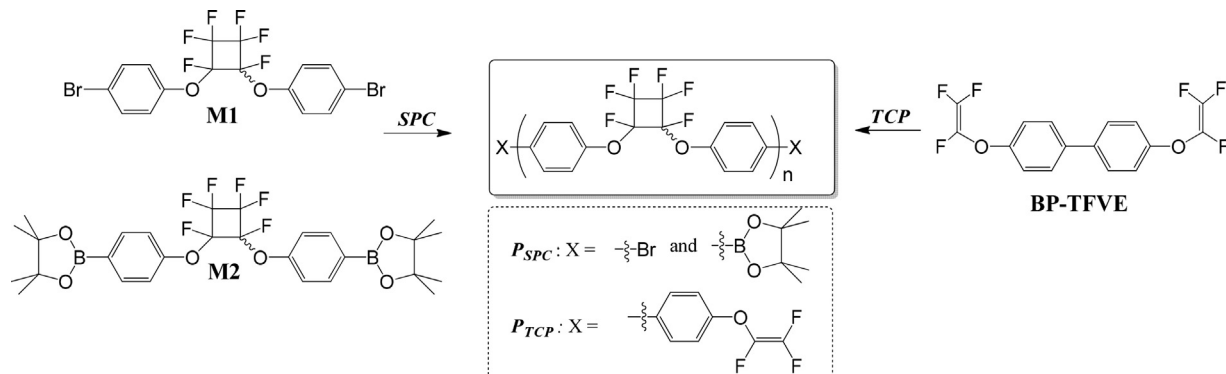
Some electro-optic (EO) chromophore-functionalized PFCB aryl ether thermosetting polymers had been prepared via [2+2] thermal cyclodimerization of their corresponding TFVE monomers (Scheme 1, Route 1) and showed very good EO properties [20,21]. However, no PFCB aryl ether polymer containing thermally stable triarylamine-based EO chromophores is reported in the

literatures due to the difficulty in the synthesis of the corresponding functional monomers. In this article, the biphenyl PFCB aryl ether polymer without any functionality was first synthesized via Suzuki polycondensation (SPC in Scheme 2). The properties of the resulting polymer P_{SPC} were compared to those of a commercially available polymer P_{TCP} used as a reference. Then PFCB aryl ether polymers containing triarylamine-based chromophores were synthesized via Suzuki polycondensation and post-polymerization modification procedures (Scheme 3). Our results show Suzuki polycondensation is suitable to prepare functional PFCB aryl ether polymers, which allows us to develop many new functional PFCB aryl ether polymers to further broaden their applications.

2. Results and discussion

2.1. Synthesis and characterization of monomers and polymers

Reactive PFCB aryl ethers **M1** and **M2** were prepared from commercially available mono-functional TFVE molecules via the thermal [2+2] cyclodimerization in good yields (Scheme S1) [22], whose structures were confirmed by ^1H NMR and ^{19}F NMR spectra. Suzuki polycondensation of these two monomers afforded a biphenyl PFCB aryl ether polymer P_{SPC} in a good yield (71%), which is analogous to the commercially available biphenyl PFCB aryl ether polymer P_{TCP} prepared via the thermal [2+2] cyclodimerization polymerization process. The number-average molecular weight (M_n) for purified polymer P_{SPC} was determined to be 5400 g/mol with a polydispersity index (PDI) of 1.7 by size exclusion chromatography (monodisperse polystyrene standards, THF as the eluent). The structure of polymer P_{SPC} was probed by ^{19}F NMR spectroscopy, which displayed characteristic PFCB spectroscopic patterns as seen in P_{TCP} (Fig. 1). The ATR-FTIR spectrum of P_{SPC} shows a broad, strong absorbance of the PFCB ring breathing mode appeared at 960 cm^{-1} (Fig. S1). Both ^{19}F NMR and ATR-FTIR results indicated that the PFCB ring in the monomers did not participate in significant side reactions during Suzuki polycondensation process. Polymer P_{SPC} has different end groups with polymer P_{TCP} (Scheme 2). The end groups of polymer P_{TCP} are aryl TFVE groups shown in its ^{19}F NMR spectrum (the characteristic pattern at ~ -119 , -126 , and -134 ; Fig. 1). Polymer P_{SPC} has two different end groups: the bromine end group and the boronate ester end group (Scheme 2). The ^1H NMR spectrum of polymer P_{SPC} shows a small signal at 1.26 ppm, which is associated to the hydrogen atoms of boronic perco-ester end groups (Fig. S2). The results from thermogravimetric analyzer/mass spectrometer (TGA-MS) studies show that polymer P_{SPC} also contains some bromine end groups (Fig. S6). Due to containing two different end



Scheme 2. Two synthetic routes to biphenyl PFCB aryl ether polymers: Suzuki polycondensation (SCP) and thermal [2+2] cyclodimerization polymerization (TCP). End groups (X) vary as a function of the polymerization route.

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