

# Chemistry of Aryl Trifluorovinyl Ethers

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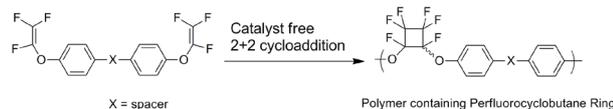
## Introduction

Fluorine-containing polymers are one of the new and exciting research directions within the polymer science programme at the University of Auckland. In the plastics world, fluorine-containing polymers represent a rather specialised group of polymeric materials. Since the accidental invention of a bizarre white powder material (It was Teflon as we know today) by a DuPont scientist during his ongoing research on new refrigerant in 1938,<sup>1</sup> the production of fluoropolymers has grown to reach an estimated world demand of 235,000 metric ton in 2011.<sup>2</sup> Their many attributes include remarkable thermal and chemical attack inertness, solvent resistance and outstanding electrical properties. These properties offset their higher cost and greater difficulty in processing than is the case for most other non-fluorinated thermoplastics.

**Table 1.** Common fluorinated alkenes used in the production of fluoropolymers

Fluorinated Alkenes	Fluoropolymers
$\text{CF}_2=\text{CF}_2$	Poly(tetrafluoroethylene) PTFE
$\text{CF}_2=\text{CFCl}$	Poly(chlorotrifluoroethylene) PCTFE
$\text{CH}_2=\text{CF}_2$	Poly(vinylidene fluoride) PVDF
$\text{CF}_3\text{CF}=\text{CF}_2$ and $\text{CF}_2=\text{CF}_2$	Copolymer of hexafluoropropylene and tetrafluoroethylene (FEP)
$\text{CF}_3\text{CF}_2\text{CF}_2\text{-O-CF}=\text{CF}_2$ and $\text{CF}_2=\text{CF}_2$	Copolymer of perfluorovinylether and tetrafluoroethylene (PFA)

Fluoropolymers are typically made from the free radical polymerization of fluorinated alkenes.<sup>3</sup> Table 1 lists the most common monomers that are currently used in the manufacture of fluoropolymers. Unlike these polymers (prepared by free radical initiated polymerization), this article introduces a unique class of semi-fluorinated polymer containing perfluorocyclobutane (PFCB) ring structure (Scheme 1).<sup>4</sup> Linear thermoplastic PFCB polymers are prepared by [2+2] cycloaddition of a single molecule containing two aryl trifluorovinyl ether (Ar-O-CF=CF<sub>2</sub>) groups following step growth kinetics. The synthesis and characterization of aryl trifluorovinyl ethers by different methods will be discussed.

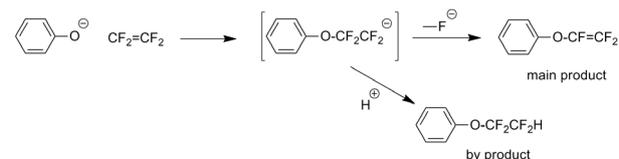


**Scheme 1.** Synthesis of perfluorocyclobutane polymers via [2+2] cycloaddition of aryl trifluorovinyl ethers

## Synthesis of Aryl Trifluorovinyl Ether (Ar-O-CF=CF<sub>2</sub>)

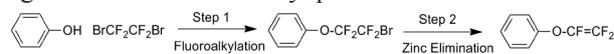
Aryl trifluorovinyl ethers can be prepared by several methods. In 1966 phenyl trifluorovinyl ether was obtained

by the reaction of an alkali metal phenoxide (PhONa or PhOK) with tetrafluoroethylene in Parr bombs.<sup>5</sup> The yield of the reaction was mediocre because of the side reaction, where the reactive fluorocarbanions are trapped by the available proton donors in the reaction system to give saturated 1,1,2,2-tetrafluoroethyl phenyl ethers (Scheme 2).



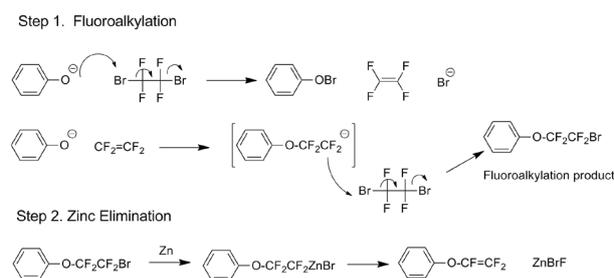
**Scheme 2.** Synthesis of phenyl trifluorovinyl ether using tetrafluoroethylene

A more efficient and mild way to prepare this compound in two step process (Scheme 3) was reported in 1993.<sup>6</sup> Starting from phenolic precursors, the first step is the fluoroalkylation with 1,2-dibromotetrafluoroethane (BrCF<sub>2</sub>CF<sub>2</sub>Br) to give 2-bromotetrafluoroethyl aryl ethers. In this reaction BrCF<sub>2</sub>CF<sub>2</sub>Br (widely used as non-toxic fire extinguishing agent) served as a fluoroalkylation agent and as a trifluorovinyl precursor.



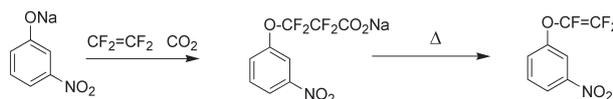
**Scheme 3.** Preparation of aryl trifluorovinyl ether using 1,2-dibromotetrafluoroethane

In contrast to the well-known alkylation paths, namely, S<sub>N</sub>1 and S<sub>N</sub>2, the fluoroalkylation reaction was rationalized by an unusual ionic chain mechanism.<sup>7</sup> As shown in Scheme 4, the reaction was initiated with the direct attack of electron-positive bromine (δ<sup>+</sup>) on the BrCF<sub>2</sub>CF<sub>2</sub>Br by phenoxide. Tetrafluoroethylene (CF<sub>2</sub>=CF<sub>2</sub>) was generated in-situ after loss of bromide anion. The phenoxides added to the CF<sub>2</sub>=CF<sub>2</sub> to give the reactive fluorocarbanions, which were quickly terminated by bromide to form 2-bromo-tetrafluoroethyl aryl ethers. In the elimination step, zinc inserted into C-Br bond of 2-bromo-tetrafluoroethyl aryl ethers in a similar way to the preparation of Grignard reagent. Finally, the aryl trifluorovinyl ethers were obtained by the elimination of ZnBrF salt at elevated temperature.



**Scheme 4.** Postulated fluoroalkylation and zinc elimination mechanism.<sup>7</sup>

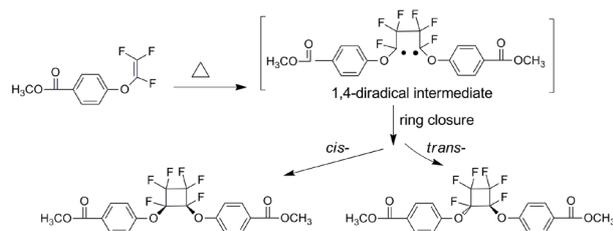
Although the above-mentioned 1,2-dibromotetrafluoroethane procedure was satisfactory for most phenolic compounds, for the deactivated phenols, such as those that are perfluorinated or that have strong electron-withdrawing groups, the reaction gave an extremely poor yield in the zinc elimination step, i.e., the zinc insertion product (Ar-O-CF<sub>2</sub>CF<sub>2</sub>-ZnBr) exhibited unusual stability. A new synthetic pathway to aryl trifluorovinyl ethers (Scheme 5)<sup>8</sup> involved the reaction of nitrophenoxide with tetrafluoroethylene and carbon dioxide to give 3-nitrophenoxy-2,2,3,3-tetrafluoropropionic acid salt. The salt was then heated up to decarboxylation temperature at 250 °C to afford the nitrophenyl trifluorovinyl ether in 46% decent yield.



**Scheme 5.** Nitrophenyl trifluorovinyl ether synthesized by Feiring *et al.*<sup>8</sup>

### Cyclodimerization of Aryl Trifluorovinyl Ether

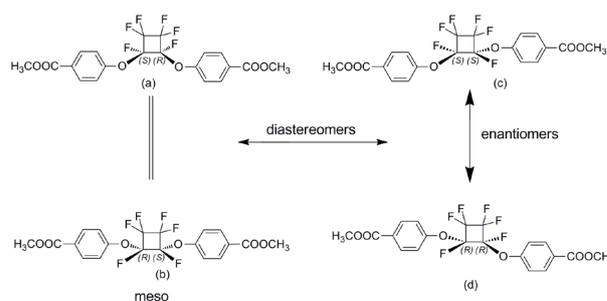
Cyclodimerization of fluorinated alkenes was observed as early as 1947 during the pyrolysis study of polytetrafluoroethylene (PTFE).<sup>9</sup> The ability of fluorinated alkenes to dimerize with themselves has been attributed to the energy relief of fluorinated double bond strain.<sup>6</sup> In the same fashion, the aryl trifluorovinyl ether groups (Ar-O-CF=CF<sub>2</sub>) underwent thermally activated [2+2] cycloaddition to form bisaryloxy substituted perfluorocyclobutane (PFCB) rings. Scheme 6 depicts the model reaction of cycloaddition of aryl trifluorovinyl ethers. The thermal cyclodimerization of methyl 4-(trifluorovinyl)oxybenzoate was carried out at 180 °C in the bulk for 12 hours under N<sub>2</sub>. The dimer was crystallized from methanol to give a white solid in 75% yield.<sup>10</sup>



**Scheme 6.** Model reaction of [2+2] cyclodimerization of aryl trifluorovinyl ethers

According to the Woodward-Hoffman rule, thermally activated [2+2] cycloaddition took place in a non-concerted manner: the initial addition of one aryl trifluorovinyl ether to another with predominantly head-to-head regioselectivity gave a 1,4-diradical intermediate, followed by ring closure to form the 1,2-disubstituted perfluorocyclobutane (PFCB) ring. About equal amounts of the cis- and trans- stereoisomers were formed.

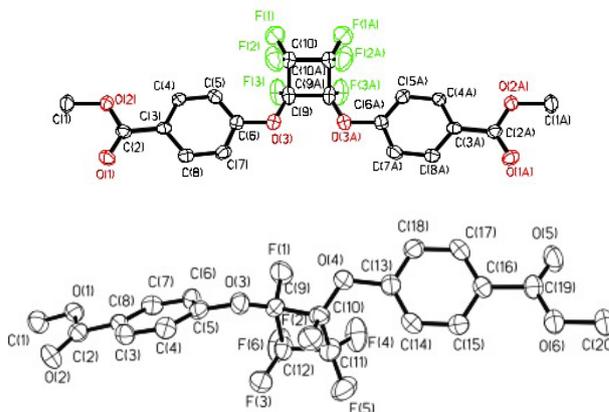
Further analysis of the products from cyclodimerization revealed that each cis- and trans- stereoisomer have two enantiomers. As can be seen in Scheme 7, the cis- product has two enantiomers (a) and (b), being (S, R) and (R, S)



**Scheme 7.** Stereoisomerism of diester.<sup>10</sup>

configuration respectively, according to the Cahn-Ingold-Prelog priority rules. Both the cis- enantiomers are meso compounds and optically inactive. The trans- product also has two enantiomers, being (S, S) and (R, R), which exist as non-superimposable mirror images of each other.

Single crystals of cis- and trans- perfluorocyclobutane diester isomers were successfully isolated from the dimer mixture. Figure 1 illustrates the single crystal X-ray structures of cis- and trans- diesters, which provide the best evidence of perfluorocyclobutane ring structure and cis-/trans- isomerization. The cis- diester has a mirror plane of symmetry, with the PFCB ring being located perfectly in a same plane. For the trans- diester, on the other hand, the PFCB ring actually is not planar, having a dihedral angle of 162.86°.



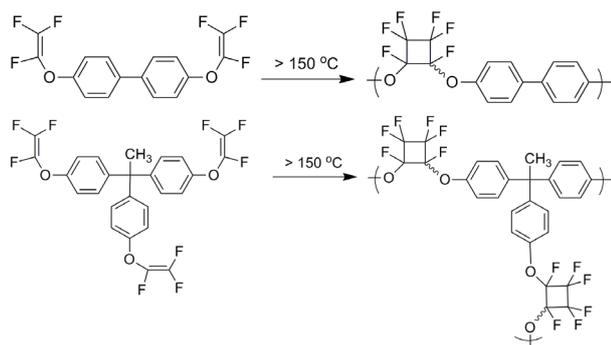
**Fig. 1.** Perspective drawing showing 50% thermal ellipsoids of diester single crystals, cis- (top) and trans- (bottom) stereoisomers.

### Polymer Synthesis via [2+2] Cycloaddition of Aryl Trifluorovinyl Ethers

The model reaction above shows that aryl trifluorovinyl ethers have unique synthetic utilities in polymer formations. Perfluorocyclobutane (PFCB) ring-containing polymers with various macromolecular architectures (such as linear, branched and cross-linked) can be prepared by [2+2] cycloaddition of a single molecule containing multiple aryl trifluorovinyl ether groups. Typically, a PFCB polymer can be prepared by simply heating the aryl trifluorovinyl ether monomers in bulk or in solution above 150 °C. The PFCB backbone contains equal numbers of randomly distributed cis- and trans- 1,2-disubstituted hexafluorocyclobutanes. Therefore, most PFCB polymers are amorphous in nature with highly optical transparency

owing to catalyst-free polymerization processes. PFCB polymers have excellent solution processability in common organic solvents and glass transition temperatures of 120 – ~350 °C.

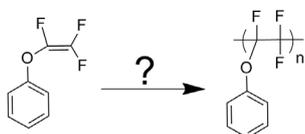
Since the phenolic compounds are accessible, PFCB polymers can easily incorporate a wide range of functional groups. Initially developed for aerospace and microelectronics applications at Dow Chemical,<sup>6</sup> PFCB polymers have received considerable attention as a versatile material for photonic applications,<sup>11-12</sup> quantum dot matrix,<sup>13</sup> hole transport materials for OLED<sup>14-15</sup> and as cross-linking groups in electro optic chromophores.<sup>16</sup> Scheme 8 shows two commercial examples of thermoplastic and thermosetting PFCB polymers.<sup>6</sup>



**Scheme 8.** Commercial examples of PFCB polymers

## Other Attempts on Polymerization of Aryl Trifluorovinyl Ether

Besides the successful cyclopolymerization of aryl trifluorovinyl ethers, other polymerization techniques were attempted to polymerize the aryl trifluorovinyl ethers. For example, benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) were used as free radical initiators to polymerize the aryl trifluorovinyl ether at the temperature below its cyclodimerization threshold (Scheme 9). However, they all appeared to be ineffective in producing polymers of high molecular weight. The results were unexpected when compared to the common fluorinated alkenes listed in Table 1, which are all polymerizable under free radical initiated polymerization conditions.



**Scheme 9.** Chain growth polymerization of aryl trifluorovinyl ether

Clearly, the free radical propagating species of aryl trifluorovinyl ethers are not stable. Aryl trifluorovinyl

ethers also show no sign of photoreactivity under UV radiation.

## Conclusions

In this review, various synthesis routes for aryl trifluorovinyl ether are discussed. Perfluorocyclobutane (PFCB) polymers are prepared via thermally activated [2+2] cycloaddition of aryl trifluorovinyl ether monomers. The cyclodimerization proceeds in a stereo-random fashion, giving roughly equal distribution of cis- and trans- stereoisomers. PFCB technology can serve as a versatile materials platform for many industrial applications. At present, free radical initiated polymerizations for aryl trifluorovinyl ethers are not successful. This is an area our laboratory has already initiated further work.

## Acknowledgements

I started the aryl trifluorovinyl ether synthesis and its polymerization when I joined Clemson University for PhD studies in 2001. I express my sincere gratitude to my research advisors and mentors at Clemson, including Dr. Dennis W. Smith Jr., Dr. Stephen H. Foulger, Dr. John Ballato, Dr. Earl Wagener and Dr. Darryl DesMarteau .

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