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Ethylene-tetrafluoroethylene (ETFE) cotelomer iodides and their transformation to surface protection intermediates

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ABSTRACT

A new class of fluorotelomers was synthesized via the cotelomerization of ethylene and tetrafluoroethylene (TFE) with 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl iodides. The telomerization led to ethylene-tetrafluoroethylene (ETFE) cotelomer iodides with the incorporation of ethylene and TFE in the cotelomer chain in an alternating fashion. By controlling the reaction parameters such as total pressure, temperature, feed ratio of the monomers, initiator feed, and conversion rate, eight-carbon cotelomer iodide or higher cotelomers could be produced preferably. The ETFE cotelomer iodides were transformed to a variety of intermediates such as alcohols, azides, amines and thiols, precursors useful to make surface modification agents.

1. Introduction

Perfluorinated telomer iodides are important intermediates and widely used for commercial production of surface protection agents for a variety of surfaces such as textiles, leather, carpet, paper, stone & tile, and for highly efficient surfactants [1,2]. Most commercially available fluorinated materials used towards repellency or surfactancy applications contain predominately eight or more carbons in their perfluoroalkyl chains. While these materials offer superior performance, concerns have been raised about the environmental fate of long chain fluorochemicals, especially their adverse bioaccumulation potential [3]. It is our interest to develop highly efficient, potentially non-bioaccumulable alternatives for surface protection and surfactancy applications. Introduction of hydrocarbon alkylene functionalities to interrupt the perfluoroalkyl chain of perfluorinated telomers may lead to likely non-bioaccumulable alternatives. For example, vinylidine fluoride incorporated telomers were suggested as possible non-bioaccumulable intermediates and surface protection agents derived from these intermediates were shown to provide good surfactant and repellent properties [4–7].

Polytetrafluoroethylene (PTFE) is a crystalline polymer with a degree of crystallinity of 40–70% and surface tension of 18.5 mN/m. The crystallinity is attributed to the ability of the fluoroalkyl chains to aggregate and self-organize. This phenomenon is seen in pefluoroalkyl telomers (8 carbon or more) and the polymers derived from them [8]. In the search of a new class of fluorinated materials based on fluoro-hydrocarbon chains for surfactancy and surface protection applications, properties of PTFE (Teflon®) and its fluoro-hydrocarbon counterpart poly(ethene-*co*-tetrafluoroethylene) (Tefzel®) were compared. Tefzel® is an ethylene-tetrafluoroethylene copolymer with mainly alternating ethylene and TFE units. Properties such as degree of crystallinity, surface tension, dielectric constant and melting point of Tefzel® are closer to that of PTFE (Table 1) [9]. This resemblance in properties inspired us to investigate the possibility of ETFE cotelomer intermediates, where the telomer chain is constituted of fluorocarbon groups intercepted by hydrocarbon moieties. These fluoro-hydrocarbon entities may assemble and have the crystalline properties of Tefzel®, while CF_3 groups form organized layers at

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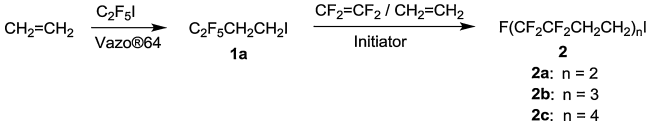
Table 1
Properties of PTFE and Tefzel®.

	Degree of crystallinity (%)	Surface tension (mN/m)	Dielectric constant	Mp (°C)
PTFE	40–70	18.5	2.1	327
Tefzel®	40–60	22.1	2.6	275



Scheme 2. Cotelomerization of TFE and ethylene with 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide leading to ETFE cotelomer iodides.

the surface to provide repellency. Schematic representation of PTFE and corresponding TFE telomer iodide and Tefzel® and ETFE cotelomer iodides are shown in Scheme 1.

We are interested in evaluating such ETFE cotelomer iodides and their derivatives, where the perfluorocarbon groups are intercepted by ethylene (–CH_2CH_2–) functional groups. These intermediates are expected to be fluorine efficient and are potentially non-bioaccumulable, as incorporation hydrocarbon functionality limits the occurrence of more than two continuous CF_2 fragments in the fluoroalkyl cotelomers. To our knowledge such compounds with a general structure of $R_fCH_2CH_2(CF_2CF_2CH_2CH_2)_nX$ (where R_f is a perfluoralkyl group, $n \neq 0$, X is halide or any common functional group) are practically unknown. The only known compounds with these general structures are $C_2F_5CH_2CH_2CF_2CF_2CH_2CH_3$ and $C_2F_5CH_2CH_2CF_2CF_2CH_2CH_2C_2F_5$. However, these compounds are not obtained via telomerization and instead prepared in poor yield via the addition of perfluoroethyl iodide to $CH_2 = CHC_2F_4CH = CH_2$, followed by reduction [10]. In this paper, we discuss the cotelomerization of ethylene and TFE with perfluoroalkylethyl iodide leading to new class of fluorotelomers [ETFE cotelomer iodides]. The fluorotelomers, thus generated herein, would be useful intermediates for a variety of applications including the development of various surface protection chemicals and surfactants.

2. Results and discussion

2.1. Cotelomerization

Telomerization of alkenes is well-known reaction. Many telomers, such as TFE telomers [11–14], CTFE telomers [15–17], vinylidene fluoride telomers [18], trifluoropropylene telomers [19], and ethylene telomers [20], have been reported. On the other hand, there are very limited examples related to the cotelomerization that provide fluorinated cotelomer [21]. Some fluorinated cotelomers are synthesized via a stepwise addition process [19,22]. Cotelomerization reaction of TFE with other olefins has not been reported prior to this work. We found cotelomerization of ethylene and TFE with 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide (**1a**) under suitable conditions can lead to ETFE cotelomer iodides (Scheme 2).

1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide (**1a**) was synthesized in almost quantitative yields via the reaction of perfluoroethyl iodide with ethylene. A batch cotelomerization of ethylene and TFE was first attempted in an autoclave (shaker tube) using a radical initiator and 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide (**1a**) as telogen. The cotelomerization reaction was performed under neat conditions; however, an optional solvent (hexanes) could be used as a

Scheme 1. Schematic representation of perfluoroalkyl telomer and ETFE cotelomer.

medium if necessary. Air was completely removed by repeated cool, vacuum/nitrogen fill cycles before charging the mixture of ethylene and TFE to the pressure vessel *[Caution! Air must be removed from the system completely; See experimental part for important safety precaution for handling TFE-ethylene mixture].* A series of similar batch cotelomerization reactions were then performed at different temperatures and pressure by keeping the same amount of the reactants but varying initiators. The reaction conditions used for the cotelomerization and the initial results are summarized in Table 2. The half pressure drop time is used as an indication of the initial reaction rate for a given reaction. The final pressure of the reaction provided an indication of the extent of a reaction (closely associated with the conversion of the reagents used in the reaction). After the completion of the reaction, unreacted iodide **1a** was removed by reduced pressure distillation, and the products were analyzed via GC–MS. The products (crude ETFE cotelomer iodides) obtained from cotelomerization constitutes alternately inserted ETFE cotelomer iodides (such as **2a**, **2b** and **2c**) as major components, and small amounts of mis-inserted cotelomer iodides (resulting from the insertion of two or more molecules of the same alkene next to each other) and additional by-products which could possibly be longer chain cotelomer iodides, products derived from the initiator or possible radical combination products. At lower reaction temperature, using Luperox® 231 as an initiator, the cotelomerization reaction was slower (indicated by longer time required for the pressure to drop by half), leading to a poor conversion as indicated by higher final pressure and larger quantities of recovered **1a** (entries 2–4, Table 2). Also, at lower reaction temperatures, it was noted that slightly more **2a** was formed as compared to **2b.** At 80 °C, using Vazo®64 initiator led to lowest initial rate and yield (entry 6), whereas, using lauroyl peroxide under similar conditions gave highest initial rate and yield (entry 5). From these batch reactions, the ratios of **2a**/**2b** remained within a narrow range of 1.7 to 2.7. As indicated by the final pressure in Table 2, varying amounts of unreacted ethylene and TFE were present at the end of the reaction period. No attempt was made to recover the unreacted ethylene and TFE. Also, starting material **1a** is volatile and may not be completely recovered (note a, Table 2). Therefore in general, only 75–80% of reaction mass was recovered after the reaction. In the very conversion reaction (entry 4, Table 2), only about 65% materials were recovered.

The batch (shaker tube) cotelomerization described above demonstrated the successful preparation of ETFE cotelomer. In order to further study the impact of other variables, such as gas composition and total pressure, the cotelomerization was also carried out in semi-batch mode, where the initiator, TFE, and ethylene were allowed to feed independently throughout the reaction as desired. Total reaction pressure was controlled by feeding gases when the reagents were consumed. Lauroyl peroxide was chosen as an initiator for semi-batch cotelomerization because of the higher reaction rate observed during the batch reaction. In addition, lauroyl peroxide also has good solubility in **1a**, and could be delivered as a solution using a syringe pump. In the semi-batch process, iodide **1a** was charged to the reactor with or without an initiator before the vessel was sealed. Ethylene and TFE were then charged to the reactor from separate feeds to a desired composition