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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 fluorohydrocarbon entities may assemble and have the crystalline properties of Tefzel®, while CF_3 groups form organized layers at

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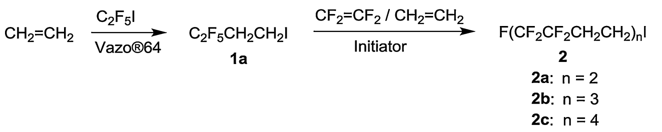
Table 1
Properties of PTFE and Tefzel®.

	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.

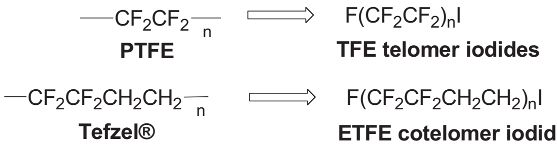
We are interested in evaluating such ETFE cotelomer iodides and their derivatives, where the perfluorocarbon groups are intercepted by ethylene ($-CH_2CH_2-$) functional groups. These intermediates are expected to be fluorine efficient and are potentially non-bioaccumulable, as incorporation hydrocarbon 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 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 constitute~~s~~ 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.



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

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

Table 2
Results from batch cotelomerization reaction of **1a** (45 g), ethylene (6 g), TFE (25 g), initiator (1.2 g) with total reaction time of 20 h.

Entry	Initiator	Temp. (°C)	Time for half pressure drop (min)	Final Pressure (psig)	Recovered[a] **1a** (g)	Total weight of products[b] (g)	**2a**/**2b**
1	Luperox® P	110	60	61	11.8	49	2.0
2	Luperox® 231	90	60	122	13.6	45.7	1.9
3	Luperox® 231	80	100	143	14.4	43	2.2
4	Luperox® 231	70	>1200	200	20	30	2.7
5	Lauroyl peroxide	80	45	65	11.4	48.2	2.4
6	Vazo®64	80	360	93	20.4	36.5	1.7

[a] **1a** is very volatile and readily escapes when the system is open to atmosphere, therefore, the recovered **1a** is not necessarily the exact same as the remainder from the reaction.

[b] Total weight of products after the removal of **1a**.

and total pressure. After the reactor was heated to a chosen reaction temperature, the total pressure was adjusted as needed by adding more TFE and ethylene. The initiator feed may start at this stage if no initiator was charged at the beginning. In experiments where the initiator was charged at the beginning (before the reactor was closed), additional initiator feed was delayed for a few hours or no further initiator was added during the reaction. TFE and ethylene were fed to the reactor constantly either at the same ratio as the initial feeds or at a different ratio to maintain the desired total pressure throughout the reaction. The details of various reaction conditions used for the semi-batch cotelomerization are summarized in Table 3. The results and GC analysis of the crude product resulting from these semi-batch cotelomerization are summarized in Tables 4 and 5. The semi-batch cotelomerization reaction was slow (indicated by low gas uptake) and gave low conversion (54% recovery of **1a**) when performed under low total pressure of 60 psig (entry 1 in Tables 3 and 4). However, under these conditions, the reaction gave good selectivity to **2a** over **2b**. We increased the total pressure to 190 psig (entry 2, Table 3), the maximum pressure of a TFE and ethylene mixture for our system to be operated safely, resulting a faster reaction and higher conversion (14% recovery of **1a**). The selectivity between **2a** and **2b** became about equal, and in addition, a large amount of **2c** was formed (entry 2, Table 5). Another experiment was then performed under the same total pressure as described in entry 2, but using less amount of initiator, larger amount of **1a**, and shorter reaction time (entry 3, Table 3). As expected a low conversion (57% recovery of **1a**) with good selectivity to **2a** over **2b** was the result (entry3, Table 4). In order to further improve the reaction rate and selectivity, we investigated increased gas feed molar ratio of TFE/ethylene to 73:27 at a reduced relative amount of initiator (compared to total **1a** used), (entry 4, Table 3). The reaction proceeded at very high rate with very low conversion (71% recovery of **1a**), and excellent selectivity to **2a** over **2b** (entry 4, Table 4). We then investigated semi-batch cotelomerization reactions under lower reaction temperature and at 160 psig or lower total pressure (entries 5–7, Table 3) with no pre-charged initiator. In these experiments, the initiator was charged only after the reaction reached the desired temperature and after total pressure was established. Gas feed ratio of TFE/ethylene (73:27) was used to establish initial total pressure, and then the feed ratio was switched to 1:1 to maintain the total pressure during the reaction. At 150–160 psig total pressure and about 70 °C, the reaction (entries 5 and 6, Tables 3 and 4) afforded good rate and good selectivity to **2a** over **2b,** and good selectivity of perfectly alternating cotelomers (**2a**, **2b**, and **2c**) over mis-inserted cotelomers (entries 5 and 6, Table 5). It is also worth to note that only a small amount of the initiator was needed for this cotelomerization reaction as described in entry 6, where the reaction was performed using 1000 ppm of initiator. Thus, by controlling the reaction parameters such as monomer feed, initiator feed, conversion rate and temperature, the ratio of the cotelomer chain length was tuned to provide preferably 8 carbon iodide or higher cotelomers, where ethylene and TFE incorporated in an alternative fashion.

The reaction mixture obtained from the semi-batch cotelomerization reactions described in Table 3 was analyzed by GC–MS. Table 5 summarizes GC analysis of the reaction mixture after

Table 3
Reaction conditions for various semi-batch cotelomerization reactions.

Entry	Initially charged (before close of the reactor) (g)		Total Pressure (psig), TFE/Ethylene (T/E) mole ratio		Lauroyl peroxide (g) in **1a** (g) added during the course of reaction/addition frequency (mL/min)	Temp (°C)	TFE charged	Ethylene charged	Reaction time (h)
	1a	Lauroyl peroxide	Initially charged at room temp.	Charged after reaching reaction temp. to adjust and maintain pressure					
1	518	11.0	20, 53/47	60, 53/47	3.3, 82/0.2[a]	75	86	16	7.5
2	518	11.0	60, 53/47	190, 53/47	1.9, 45/6[a]	75	397	97	10.5
3	999	6.0	60 psig, 53/47	190, 53/47	0	75	151	38	4.5
4	1997	7.9	60 psig, 73/27	160, 73/27	0	75	299	29	4.5
5	850	0.0	60 psig, 73/27	Adjust: 160, 73/27 Maintain: 160, 50/50	3.2, 119/1[b]	70	330	67	14
6	1905	0.0	60 psig, 73/27	Adjust: 150, 73/27 Maintain: 150, 50/50	2, 67/5[c]	70	364	70	16
7	1398	0.0	50 psig, 73/27	Adjust: 100, 73/27 Maintain, 100, 50/50	7.5, 225/5[d,e]	70	512	96	42

[a] Initiator addition started 3 h after the start of reaction.

[b] Added when system reached 160 psig.

[c] Added when system reached 150 psig.

[d] 5 mL/min for first 5 min then added through the reaction.

[e] addition started when system reached 100 psig.

Table 4
Results from the cotelomerization of TFE and ethylene with **1a**.

Entry	Recovered **1a** (%)	Total solid products (g)	TFE uptake in first 30 min (g)	**2a**/**2b** (GC area)
1	54	212	11	5.1
2	14	827	32	1
3	57	370	20	4.6
4	71	537	110	8.2
5	42	773	41	2.6
6	66	841	38	4.5
7	50	1150	9	3

removal of starting material **1a** and relative ratios for various product peaks based on GC area were listed. The GC–MS analysis reveals that in addition to the desired perfectly alternating cotelomer iodides varying amounts of mis-inserted oligomers (insertion of more than one ethylene or TFE unit inserted next each other in the cotelomer chain) were formed during the cotelomerization. The product ratios of these cotelomer iodides were influenced by various reaction parameters such as monomer feed ratio, reaction pressure, reactant and initiator concentration and reaction time. At a relatively low TFE/ethylene feed ratio (53:47) (entries 1–3, Table 3), there were no triple TFE inserted product (FTETTTEI or FTETTTETEI) and only small amounts of double TFE inserted product (FTETTEI or FTETTETEI & FTETETTEI) were detected. When TFE/ethylene gas feed ratio was increased from 53:47 to 73:27 (entry 4, Table 3), significant amount of FTETTEI, and some FTETTTEI, were observed (entry 4, Table 5). In this reaction, TFE/ethylene ratio of the gas composition in the reactor is expected to increase further during the course of the reaction as the consumption of TFE and ethylene at any given time was closer to 1:1. Higher TFE/Ethylene ratio also appeard to suppress ethylene double insertion as no FTETEEI and FTEETEI were detected, and only small amount of FTEEI was observed (entry 4, Table 5). When TFE/ethylene gas ratio was initially set to 73:27, then gas feed ratio was adjusted to 50:50 during reactions (entries 5–7, Table 3), the amount of FTETTTEI was minimized and the amount of FTETTTETEI was siginificantly reduced. In the meantime, the amounts of multiple ethylene inserted products were kept as similar or lower compared with the previous reactions (entries 1–3, Table 5). Again, higher total reaction pressure led to faster reaction rates as indicated by TFE uptake in the first 30 min during the reaction (entries 5–7, Table 4). Thus, it is demonstrated that ETFE cotelomer iodides can be prepared with good selectivity to perfectly alternating ones at good reaction rate. Formation of ETFE copolymers were not observed during the cotelomerization reaction. The mass spectrometry analysis of several representative constituents present in the reaction mixture is shown in Fig. 1. All the coteleomer iodides contain an end group alkyl iodide (R-CH_2CH_2I) and no products containing a fluoroalkyl iodide (R-CF_2CF_2I) end group were detected. Compounds (**2a**, **2b**, and FTEETEI), where there was a 2-carbon space between iodine and fluorinated carbons, gave large molecular ion peaks. Loss of HF appears to be common for ETFE cotelomer fragmentation. The peaks resulting from the loss of HF, showed a higher intensity, generally were the base peak. For **2a**, the peak (m/e: 197) was assigned to the fragment that was formed by breaking the CF_2–CF_2 bond in the middle of the molecule. That fragment would further lose HF to form a new fragment with m/e: 177 and 100% relative intensity. Compounds (PTEEI and FTETEEI), in which there was a 4-carbon space between iodine and fluorinated carbons, gave very small molecular ion peaks but very large peaks for the fragment of $M^+ - I$.

A proposed mechanistic explanation for the alternating insertion reaction of ethylene and TFE during cotelomerization

Table 5
GC analysis of mixtures from various semi-batch cotelomerizations.

Cotelomer		FTEEI	**2a**	FTETTEI	FTETTTEI	FTETEEI	FTEETEI	**2b**	FTETTETEI & FTETETTEI	FTETTTETEI & FTETTETTEI	FTETETEEI & isomers	**2c**	FTETTETETEI & FTETETTETEI & FTETETETTEI	Not fully identified	% Selectivity to **2a** + **2b** + **2c**
Entry	GC retention time (min)	4.5	5.0	6.1	6.9	7.0	7.1	7.5	8.3	8.9	9.1	9.4	10	11	
1	Peak area (%)	6.5	61	8.1	–	1.4	0.6	12	3.5	–	5.9	0.9	–	–	74
2		7.9	27.8	3.1	–	4	1.6	28.6	5.6	–	3.1	13	3.3	2.3	69
3		14.9	57.7	4.7	–	2.6	1.1	12.5	2	–	2.2	2	–	–	72
4		2.8	54.2	21.7	5.6	–	–	6.6	5.2	3.8	–	–	–	–	61
5		7.8	48.4	6.4	0.5	2.5	0.9	18.7	5.9	0.7	0.5	4.5	2.6	0.7	72
6		8.6	58.2	7.5	0.6	1.7	0.6	12.9	4.3	0.4	0.9	2.6	1.3	0.4	74
7		7.7	53	6.1	0.4	2.3	0.7	17.7	5.2	0.5	0.5	4.4	0.9	0.5	75

FTEEI = $C_2F_5(C_2H_4)_2I$, **2a** = $C_2F_5C_2H_4C_2F_4C_2H_4I$, **FTETTEI** = $C_2F_5C_2H_4(C_2F_4)_2C_2H_4I$, **FTETTTEI** = $C_2F_5C_2H_4(C_2F_4)_3C_2H_4I$, **FTETEEI** = $C_2F_5C_2H_4C_2F_4(C_2H_4)_2I$, **FTEETEI** = $C_2F_5(C_2H_4)_2C_2F_4C_2H_4I$, **2b** = $C_2F_5(C_2H_4C_2F_4)_2C_2H_4I$, **FTETTETEI** = $C_2F_5C_2H_4(C_2F_4)_2C_2H_4C_2F_4C_2H_4I$, **FTETETTEI** = $C_2F_5C_2H_4C_2F_4C_2H_4(C_2F_4)_2C_2H_4I$, **FTETTTETEI** = $C_2F_5C_2H_4(C_2F_4)_3C_2H_4C_2F_4C_2H_4I$, **FTETTETTEI** = $C_2F_5C_2H_4(C_2F_4)_2C_2H_4(C_2F_4)_2C_2H_4I$, **FTETETEEI** = $C_2F_5(C_2H_4C_2F_4)_2(C_2H_4)_2I$, **2c** = $C_2F_5(C_2H_4C_2F_4)_3C_2H_4I$, **FTETTETETEI** = $C_2F_5C_2H_4(C_2F_4)_2(C_2H_4C_2F_4)_2C_2H_4I$, **FTETETTETEI** = $C_2F_5(C_2H_4C_2F_4)_2(C_2F_4C_2H_4)_2I$, **FTETETETTEI** = $C_2F_5(C_2H_4C_2F_4)_3C_2F_4C_2H_4I$.

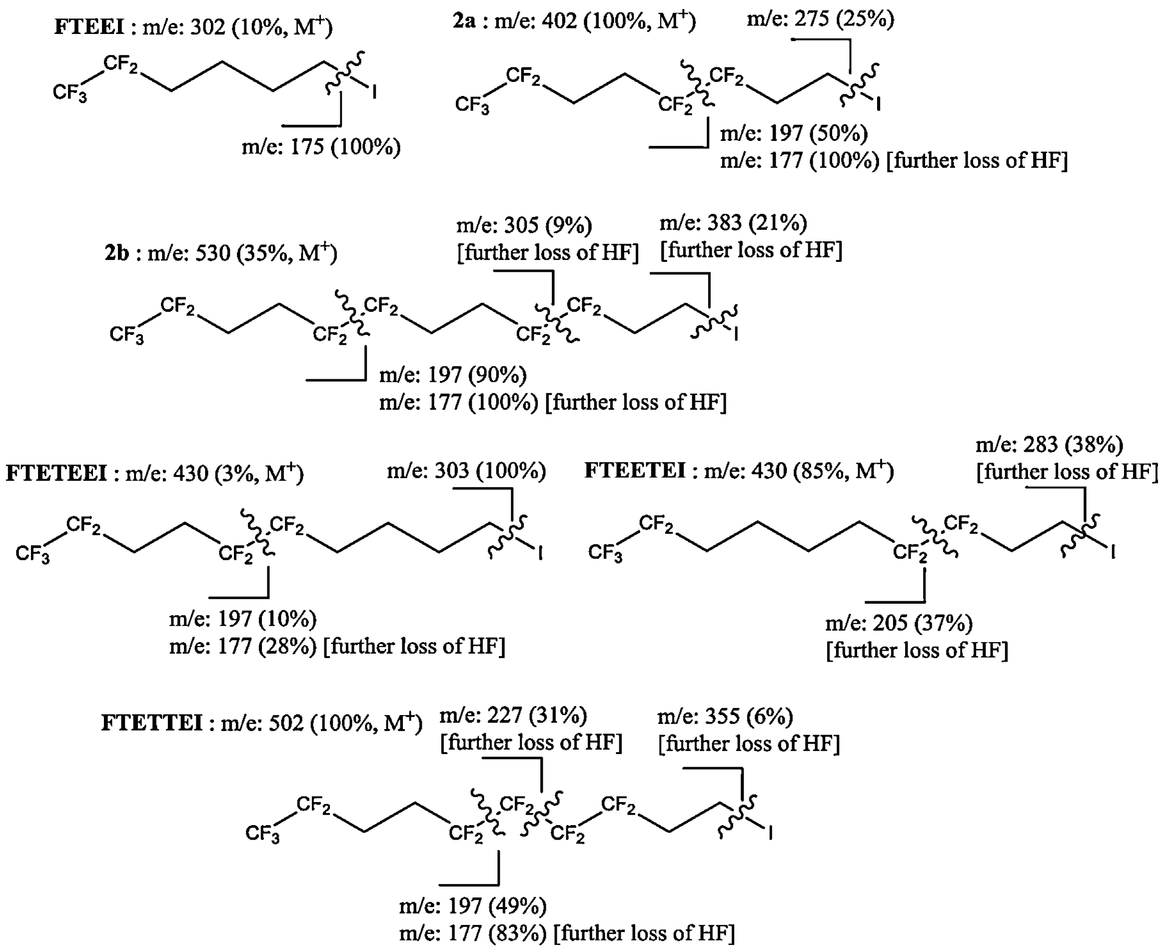
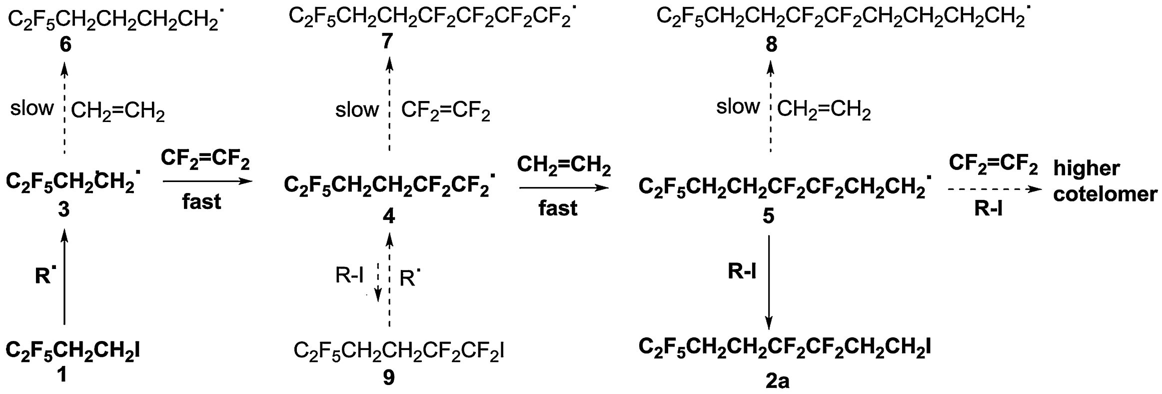


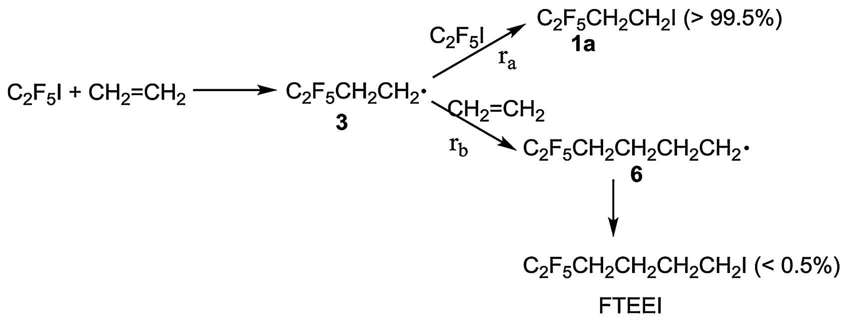
Fig. 1. MS analysis of representative ETFE cotelomers.

with 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide is presented in Scheme 3. The preferred pathway is represented in bold. A radical ($R^•$) in the system (from the initiator or other radical intermediates) reacted with the iodide (**1**) to form the hydrocarbon radical **3** which reacted with TFE faster than ethylene to form a fluorocarbon radical **4** as a major intermediate. The fluorocarbon radical **4** reacted with ethylene faster than with TFE and resulted hydrocarbon radical **5** as major intermediate species. The radical **5** further reacted with TFE faster than ethylene and the sequence continue until the radical terminates.

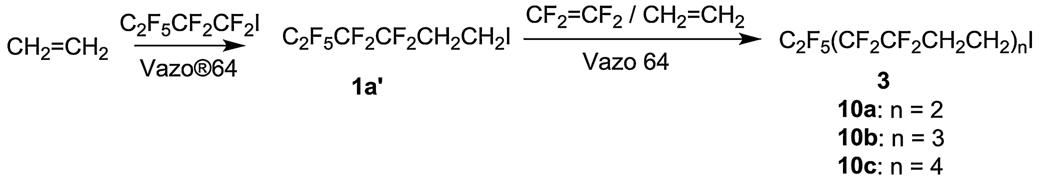
It has been reported that the $k(CF_2 = CF_2)/k(CH_2 = CH_2)$ rate ratio for addition of methyl radical ($^•CH_3$) is about 9.5, but is 0.1 for addition of trifluoromethyl radical ($^•CF_3$)[9]. This reaction rate difference between the hydrocarbon or fluorocarbon radical species and corresponding complementary olefinic species is responsible for the formation of the desired alternating ETFE cotelomers [23,24]. The intermediate radical species involved in the telomerization process can pick up an iodine atom at any stage of the reaction sequence to form the corresponding ETFE cotelomer iodides.



Scheme 3. Alternating insertion reaction during cotelomerization.



Scheme 4. Reaction pathway to form **1a** and FTEEI.



Scheme 5. Cotelomerization of TFE and ethylene with **1a**′ leading ETFE cotelomer iodides.

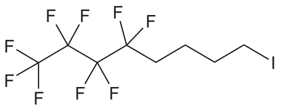
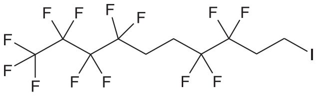
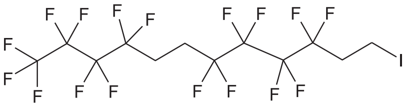
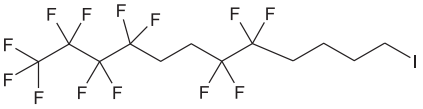
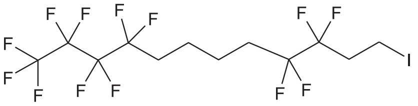
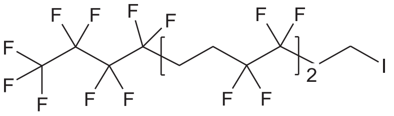
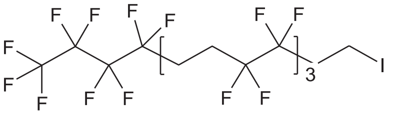
The iodides of the type **2a**, where the hydrocarbon end was terminated with iodine, were seen as the major product, and fluorocarbon iodides of the type **9** were not seen in the reaction mixture. It was speculated that fluorocarbon iodide (**9**) formed during the process was much more reactive and dissociated faster to the corresponding radical intermediate **4**, which underwent reaction through the preferred pathway with ethylene. It was consistent with the observation that reaction of pentafluoroethyl iodide with ethylene forms quantitative yield of **1a**. The impurity, ethylene double insertion product, 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorohexyl iodide (FTEEI), was about a fraction of one percent in the reaction mixture, even though the reaction was carried out under excess ethylene. Therefore, the ratio of r_a/r_b could be very large and the radical **3** reacted with pentafluoroethyl iodide much faster than with ethylene (Scheme 4). Thus, in our cotelomerization, any fluoroalkyl iodide type of **9** would quickly react with hydrocarbon radical type of **3**.

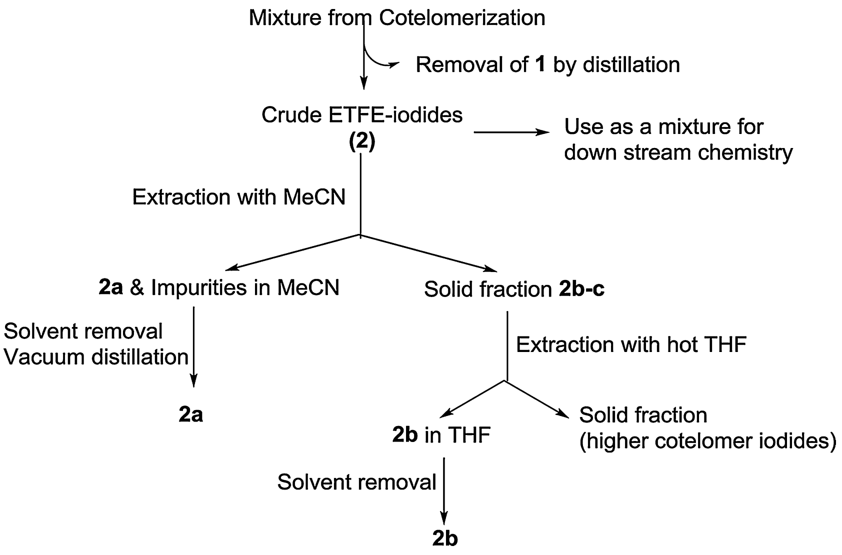
ETFE cotelomers with 1*H*,1*H*,2*H*,2*H*-perfluorohexyl iodide (**1a**′) were similarly prepared in a shaker tube, wherein, ethylene and TFE were cotelomerized with iodide **1a**′ at 80 °C using Vazo® 64 initiator for 20 h, to provide corresponding cotelomers (Scheme 5). The reaction mixture obtained from cotelomerization was analyzed by GC–MS after the removal of the unreacted **1a**′. GC area ratios of various identified products and their structure are summarized in Table 6.

2.2. Isolation of ETFE cotelomer iodides

The key cotelomers, **2a** and **2b**, were successfully isolated and characterized. Mixtures obtained from the telomerization process were subjected to distillation to remove unreacted **1a**. After removing the starting material, the crude mixture of ETFE cotelomer iodides [F($CF_2CF_2CH_2CH_2$)$_n$I] mainly constituted iodide fractions $n = 2$ (**2a**), 3 (**2b**) and small amounts of higher or mis-inserted cotelomers. This crude mixture could be used for downstream chemistry to produce surface protection intermediates. However, it is also possible to isolate individual ETFE cotelomer iodide components via fractional distillation or a selective sequence of extractions followed by distillation. The isolation process is schematically outlined in Scheme 6. Extraction of the crude mixture with acetonitrile preferentially removes ETFE cotelomer iodide **2a** along with impurities. This extract provided pure **2a** upon solvent removal followed by vacuum distillation. The solid fraction left from the acetonitrile extraction, further extracted with hot tetrahydrofuran led to a preferential extraction of ETFE cotelomer iodide **2b**. The remaining solid fraction consisted of higher ETFE cotelomer iodides. The crude ETFE cotelomer iodides (**2**) and individually isolated **2a** and **2b** were used for downstream

Table 6
Product distribution of cotelomerization of ethylene and TFE with **1a**′.

Rt	ID	GC area %	Structure of the cotelomer iodide
5.48	FBEEI	10.2	
5.95	**10a**	57	
6.84	FBETTEI	4.8	
7.74	FBETEEI	4.4	
7.80	FBEETEI	1.6	
8.15	**10b**	17	
9.92	**10c**	5.2	



Scheme 6. Isolation of ETFE cotelomers and individual components.

chemistry to develop surface protection intermediates. Similarly, from the crude product obtained from the cotelomerization of ethylene and TFE with 1*H*,1*H*,2*H*,2*H*-perfluorohexyl iodide (**1a′**), the product **10a** was isolated as a single component.

2.3. Crystalline ETFE cotelomer iodides

The crude ETFE iodides (**2**) were solid at room temperature. The individually isolated ETFE iodide components **2a** and **2b** were also solids at room temperature. The distilled **2a** was crystallized from hexane and had a melting point of 75–77 °C. In comparison, linear hydrocarbon iodide with 16 carbons ($C_{16}H_{33}I$) is still a liquid at room temperature (with mp. 22 °C) [25]. A number of eight carbon fluoroalkyl iodides containing hydrocarbon spacers [$C_6F_{13}CH_2CH_2I$, $C_4F_9(CH_2)_4I$, and $C_2F_5(CH_2)_6I$] were liquids at room temperature [20,26,27]. Other than the examples discussed here, the only other example of an 8-carbon iodide with melting point above room temperature is $C_4F_9CH_2CF_2CH_2CH_2I$ (mp. 41–43 °C), about 30 °C lower than that of ETFE cotelomer iodide, **2a** [28].

The X-ray structure revealed significant inter- and intra-molecular short contact of C–F. . .H–C (Figs. 2 and 3), that is the distances between F and H (linked by blue or red lines) are smaller than the sum of van der Waals radii of F and H atoms by more than 0.1 Å. It is believed that the individual C–F. . .H–C short contact may be weak (1–2 kJ/mol [29–31], but the sum of these short contact may be sufficient to help organizing a three-dimensional packing to yield a CF_3 layer (Fig. 4). It is known that perfluoroalkyl chains form helical structures due to electrostatic repulsion of fluorine atoms in the relative 1,3-positions on the chain [32]. However, ETFE cotelomer formed a non-helical conformation (Fig. 5), partially due to short contact between fluorine atom and hydrogen atom in the relative 1,3-positions on the chain.

2.4. Surface protection derivatives from ETFE cotelomer iodides

We were particularly interested in developing new ETFE cotelomer based surface protection derivatives analogous to various fluorotelomer derivatives. It is possible to synthesize a variety of new ETFE cotelomer based intermediates utilizing simple chemistries outlined in Scheme 7. All these derivatives could be further transformed to monomers, polymers, or surfactants useful as surface protection chemicals.

On paper, these transformations appeared simple as the well-known chemistry used for the transformation of telomer iodides to corresponding derivatives such as telomer alcohols, azides, amines, thiocaynates, thiols, sulfides, sulfonic acids, isocyanates

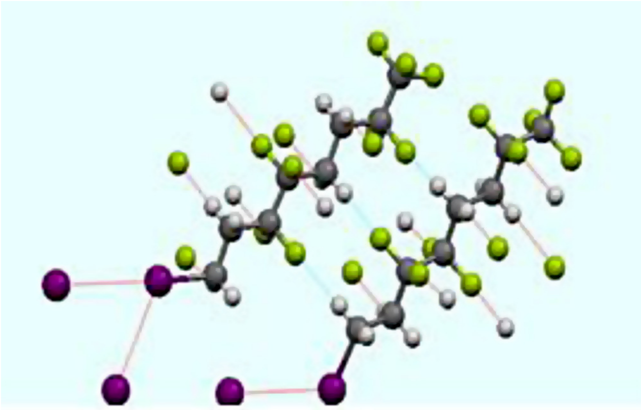


Fig. 2. Inter-molecular interactions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

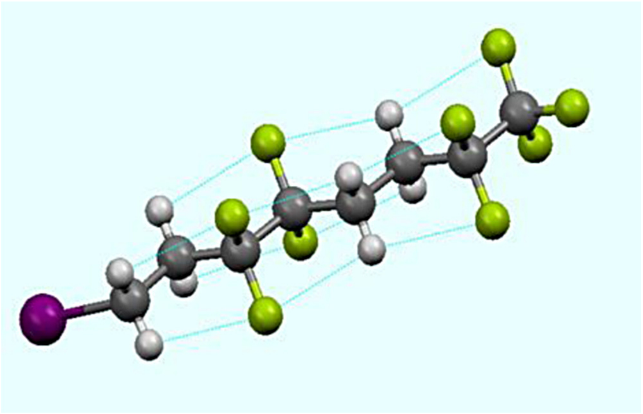


Fig. 3. Inter-molecular interactions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

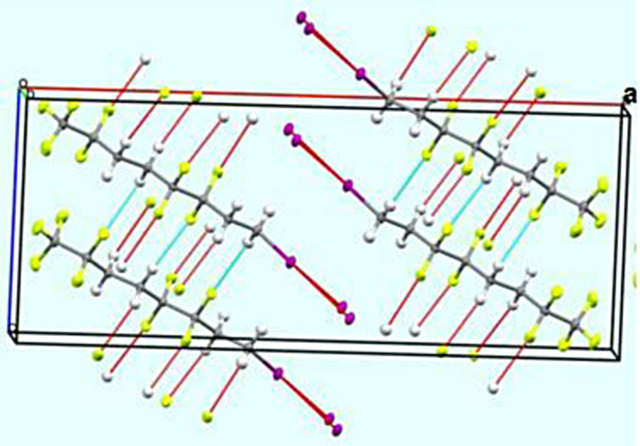


Fig. 4. Packing of iodide **2a**. The CF_3 groups form in layers around cell edges $a = 0$ and the iodines form layers around the middle of the cell at $a = 1/2$.

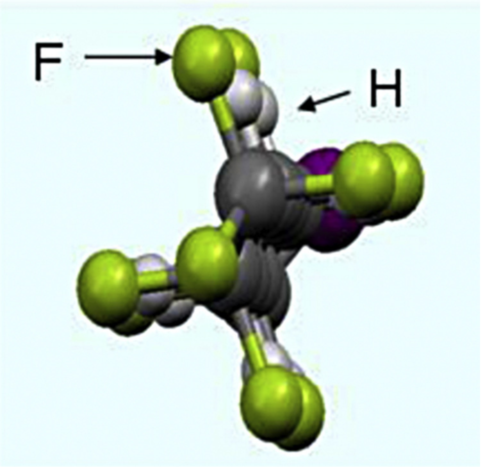


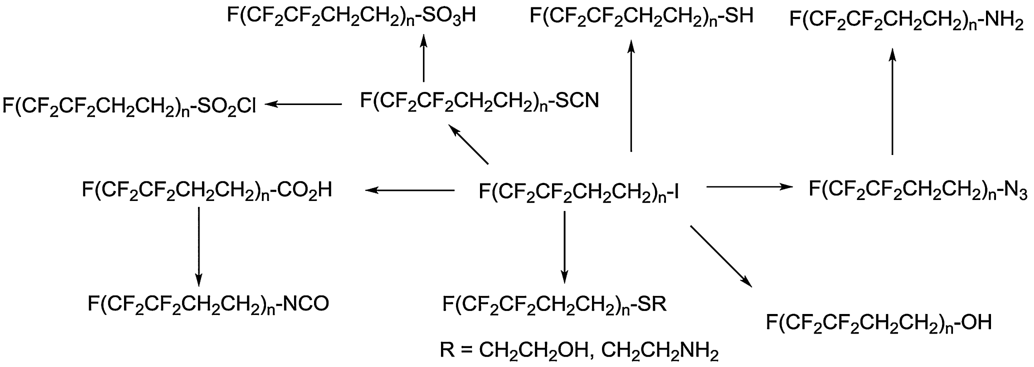
Fig. 5. Non-helical conformation of iodide **2a**.

etc. could be extended to ETFE cotelomer iodides with minor modification [33–38]. However, there are major difficulties associated with, particularly with regard to the poor solubility of the ETFE cotelomer iodides in some of the organic solvents used as medium for these transformations. So not all the transformations outlined in Scheme 7 have been attempted and a few important transformations that lead to corresponding alcohols, amines, thiocyanates, thiols, etc were performed. ETFE cotelomer iodides **2a**, **2b,** and **10a** were hydrolyzed to corresponding alcohols, **11a, 11b** and **12a**, via a reaction with *N*-methylformamide at 150 °C for 19 h followed by acid treatment in ethanol [33] or with oleum (15% SO_3) at 60 °C followed by hydrolysis as shown in Scheme 8 [34].

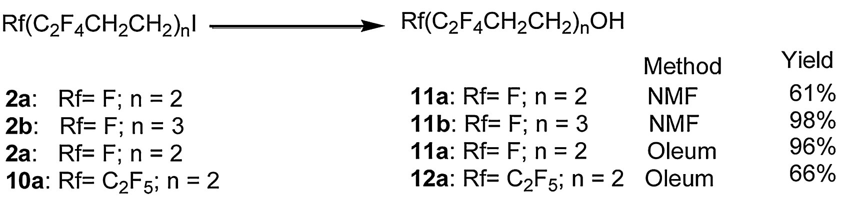
The ETFE cotelomer iodide, **2a**, was converted to the corresponding thiocyanate **13a** in high yield by the treatment with potassium thiocyanate (Scheme 8a) [35].

The crude ETFE cotelomer iodide (**2**) which contains **2a** and **2b** as major components was transformed to corresponding amine **15** via the cotelomeric azides **14** followed by reduction using hydrazine hydrate and Ni-Raney (Scheme 9). The transformation of the iodide to the azide was initially attempted under phase-transfer conditions, as described in the literature for telomer iodides [36]. However, this reaction failed to give good yield of the azide and only 10% conversion was observed. This was attributed to the poor solubility of the ETFE cotelomer iodide in the reaction medium. We then attempted this transformation using DMF, acetone or acetonitrile as solvents under heating conditions (80–90 °C), which yielded the ETFE-azides **14** in quantitative yields. The thermogravimetric analysis of the cotelomeric azides showed decomposition of the contents at 129 °C. The transformation of the azide to the amine **15** was also performed using a mixed solvent system comprising of 1:1 water and ethanol, using hydrazine hydrate/Ni-Raney to provide 87% isolated yield of the amine.

The crude ETFE cotelomer iodide (**2**) which contains **2a** and **2b** as major components was transformed to corresponding thiol **16** by refluxing with thiourea followed by basic hydrolysis of the



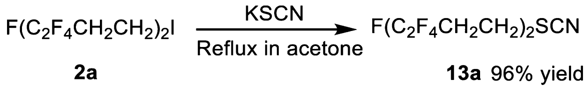
Scheme 7. Various possible transformations of ETFE cotelomer iodides.



$Rf(C_2F_4CH_2CH_2)_nI \longrightarrow Rf(C_2F_4CH_2CH_2)_nOH$

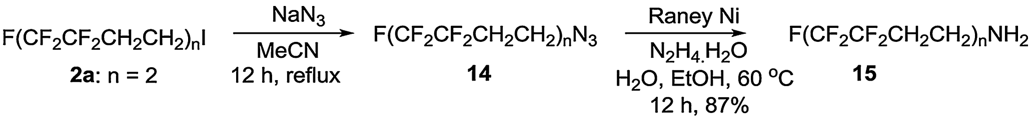
		Method	Yield
2a: Rf= F; n = 2	**11a**: Rf= F; n = 2	NMF	61%
2b: Rf= F; n = 3	**11b**: Rf= F; n = 3	NMF	98%
2a: Rf= F; n = 2	**11a**: Rf= F; n = 2	Oleum	96%
10a: Rf= C_2F_5; n = 2	**12a**: Rf= C_2F_5; n = 2	Oleum	66%

Scheme 8. Preparation of ETFE cotelomer alcohols.



$$\underset{\mathbf{2a}}{F(C_2F_4CH_2CH_2)_2I} \xrightarrow[\text{Reflux in acetone}]{KSCN} \underset{\mathbf{13a}\ 96\%\ \text{yield}}{F(C_2F_4CH_2CH_2)_2SCN}$$

Scheme 8a. Preparation of ETFE cotelomerthiocyanate.



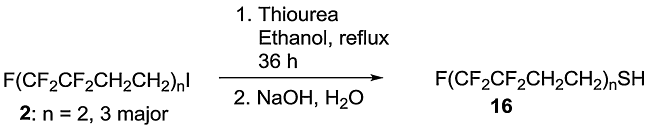
$$\underset{\mathbf{2a}:\ n = 2}{F(CF_2CF_2CH_2CH_2)_nI} \xrightarrow[\text{MeCN, 12 h, reflux}]{NaN_3} \underset{\mathbf{14}}{F(CF_2CF_2CH_2CH_2)_nN_3} \xrightarrow[\text{N}_2\text{H}_4\text{.H}_2\text{O, H}_2\text{O, EtOH, 60 °C, 12 h, 87\%}]{\text{Raney Ni}} \underset{\mathbf{15}}{F(CF_2CF_2CH_2CH_2)_nNH_2}$$

Scheme 9. Transformation of ETFE cotelomer iodides to corresponding azides and amines.

intermediate thiouronium salt using sodium hydroxide [37]. The reaction was slow in ethanol presumably due to the poor solubility of the ETFE cotelomer iodide in that solvent. However, refluxing the reaction mixture for a prolonged period of time (36 h) provided >95% conversion (Scheme 10).

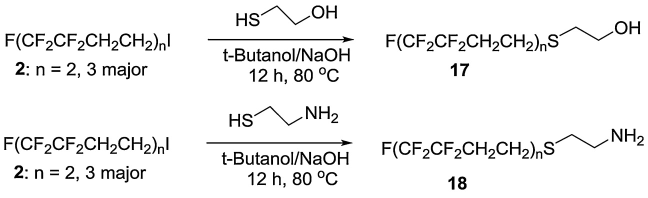
We also extended this chemistry to the synthesis of an ETFE cotelomer hydroxyethyl sulfide **17** by the displacement of ETFE cotelomer iodide with 2-mercaptoethanol in t-butanol in presence of sodium hydroxide (Scheme 11). Similarly, an ETFE cotelomer aminoethyl sulfide **18** was derived from ETFE cotelomer iodides by the displacement reaction with 2-aminoethanethiol under similar conditions. Elimination products, olefins $C_2F_5CH_2CH_2CF_2CF_2CH = CH_2$ or $C_2F_5(CH_2CH_2CF_2CF_2)_2CH = CH_2$, were not observed under these reaction conditions. The isolated yield of ETFE cotelomer hydroxyethyl sulfide **17** was 77%. Similarly, reaction of ETFE cotelomer iodides and 2-aminoethanethiol in presence of sodium hydroxide provided ETFE cotelomer aminoethyl sulfide **18** in 89% isolated yield (Scheme 11).

The ETFE cotelomer alcohols, amines, thiols, hydroxyethyl sulfides and aminoethyl sulfides could be transformed to their corresponding acrylates or acylamides, the key ingredient monomers useful for making fluoroacrylic copolymer repellents. The alcohols could also be transformed ethoxylates or phosphates or urethanes, candidates widely used as surfactants and coating additives. In addition, a variety of chemistries described on Scheme 7 could be performed to create a library of ETFE cotelomer intermediates that in turn provide surface protection agents suitable for variety of applications. In addition, the cotelomerization chemistry described here could be extended for the cotelomerization of 1*H*,1*H*,2*H*,2*H*-perfluoroalkyl iodides with ethylene and a variety of fluorinated alkenes is currently under our investigation. These intermediates are expected to be fluorine efficient and potentially non-bioaccumulable as incorporation hydrocarbon functionality limits the occurrence of more than two continuous CF_2 fragments in the ETFE cotelomers.



$$\underset{\mathbf{2}:\ n = 2,\ 3\ \text{major}}{F(CF_2CF_2CH_2CH_2)_nI} \xrightarrow[\text{2. NaOH, H}_2\text{O}]{\text{1. Thiourea, Ethanol, reflux, 36 h}} \underset{\mathbf{16}}{F(CF_2CF_2CH_2CH_2)_nSH}$$

Scheme 10. Transformation of ETFE cotelomer iodides to corresponding thiols.



Scheme 11. Transformation of ETFE cotelomer iodides to corresponding hydroxyethyl and aminoethyl sulfides.

3. Conclusions

A new class of fluorotelomers was synthesized via the cotelomerization of ethylene and 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 monomer feed, initiator feed, conversion rate and temperature, the ratio of the cotelomer chain length could be tuned to provide preferably to eight carbon iodide or higher cotelomers. Unlike TFE telomer iodides, the ETFE cotelomer iodides were crystalline solids. The ETFE cotelomer iodides were transformed to a variety of useful surface protection intermediates such as alcohols, thiocyanates, azides, amines, and thiols in high yield.

4. Experimental

4.1. General

All solvents and reagents, unless otherwise indicated, were purchased from commercial sources and used directly as supplied. TFE and perfluoroalkyl iodides were obtained from E.I. du Pont de Nemours and Company, Wilmington, DE. ^1H and ^{19}F NMR spectra were recorded on a Brucker DRX 400 or 500 Spectrometer. Chemical shifts have been reported in ppm relative to an internal reference ($CFCl_3$ or TMS). All melting points reported were uncorrected. GC analysis was performed on an Agilent 5890 using a DB 5 column and FID detector, oven temperature: hold at 50 °C for 2 min, increase 20 °C/min to 280 °C and hold at 280 °C for 5 min.

Caution! A 1:1 mixture of ethylene and TFE is extremely hazardous and may be ignited at 60 °C and >60 psig pressure. Use of such a mixture should be restricted within these limits for operation, or in an operation system (e.g. autoclave) that can withstand the peak pressure in case the mixture does ignite.

4.2. Ethylene-tetrafluoroethylene cotelomerization with 1H,1H,2H,2H-perfluorobutyl iodide under batch process

A 400 mL shaker tube was charged with 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide (**1a**, 45 g) and Vazo®64 (1.0 g). After cool evacuation, ethylene (6.0 g) and TFE (25.0 g) were added. The resulting mixture was heated to 80 °C for 20 h. The unreacted 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide was recovered by vacuum distillation at room temperature. The remaining solid was extracted with CH_3CN (3 times 100 mL). The CH_3CN extracts were concentrated and distilled at reduced pressure to give pure iodide 1,1,2,2,5,5,6,6-octahydroperfluoro-1-iodooctane. The solid remaining after CH_3CN extraction was extracted with warm tetrahydrofuran. The tetrahydrofuran extract was concentrated and dried to give 1,1,2,2,5,5,6,6,9,9,10,10-dodecahydroperfluoro-1-iodododecane. The solid remaining after tetrahydrofuran extraction was mainly iodides of formula $C_2F_5(CH_2CH_2CF_2CF_2)_n$

CH_2CH_2I (wherein $n = 3$ and higher cotelomers), which have very low solubility in common solvents.

The products 1,1,2,2,5,5,6,6-octahydroperfluoro-1-iodooctane and 1,1,2,2,5,5,6,6,9,9,10,10-dodecahydroperfluoro-1-iodododecane were characterized by ^1H NMR and ^{19}F NMR as shown below: 1,1,2,2,5,5,6,6-octahydroperfluoro-1-iodooctane: mp. 75–77 °C. ^1H NMR ($CDCl_3$) δ 2.33 (m, 4*H*, CH_2), 2.68 (m, 2*H*, CH_2), 3.24 (m, 2*H*, CH_2I). ^{19}F NMR ($CDCl_3$) δ −85.9 (s, 3F, CF_3), −115.8 (m, 4F, CF_2), −119.2 (m, 2F, CF_2).; 1,1,2,2,5,5,6,6,9,9,10,10-dodecahydroperfluoro-1-iodododecane: mp. 125–128 °C. ^1H NMR (acetone-d6) δ 2.46 (m, 8*H*, CH_2), 2.77 (m, 2*H*, CH_2), 3.37 (m, 2*H*, CH_2I). ^{19}F NMR (acetone-d6) δ −86.7 (bs, 3F, CF_3), −117.1 (m, 6F, CF_2), −117.3 (m, 2F, CF_2), −119.5 (m, 2F, CF_2).

*4.3. Ethylene-tetrafluoroethylene cotelomerization with 1*H*,1*H*,2*H*,2*H*-perfluoroethyl iodide under semi-batch process.*

A one gallon reactor was charged with 1*H*,1*H*,2*H*,2*H*-perfluorobutyl iodide (**1a**, 850.0 g). After cool evacuation, TFE/ethylene in a ratio of 73:27 were added until pressure reached 60 psig. The reaction was then heated to 70 °C. More TFE and ethylene in a ratio of 73:27 were added until pressure reached 160 psig. A lauroyl peroxide solution (4.0 g lauroyl peroxide in 150.0 g of **1a**) was added in 1 mL/min rate. Gas feed ratio was adjusted to 1:1 of ethylene and TFE and the total pressure was kept at 160 psig. The initiator feed was stopped after about 1 h and total about lauroyl peroxide (3.2 g) in of **1a** (119.0 g) was added to the reaction. After about 67.0 g of ethylene was added, both ethylene and TFE feeds were stopped. The reaction was heated at 70 °C for another 8 h. The volatiles were removed by vacuum distillation at room temperature. A solid of the ETFE cotelomer iodides **2** (773.0 g) was obtained.

*4.4. Cotelomerization of ethylene and TFE with 1*H*,1*H*,2*H*,2*H*-perfluorohexyl iodide under batch process*

A 400 mL shaker tube was charged with 1*H*,1*H*,2*H*,2*H*-perfluorohexyl iodide (**1a**′, 75.0 g), Vazo® 64 (1.5 g). After cool evacuation, ethylene (6.0 g) and TFE (25.0 g) were added. The resulting mixture was heated to 80 °C for 20 h. A wet solid was obtained. Combined reaction mixtures from 8 identical cotelomerization experiments were distilled under vacuum to recover unreacted **1a**′ at room temperature. The remaining solid was then extracted with acetonitrile (4 × 750 mL). The combined acetonitrile extracts were concentrated to give a solid (418.6 g), which was further distilled at reduced pressure to give purer product (>90% purity, and major impurities in this product were FBEEI, FBETTEI, and FBETEEI), $C_2F_5(C_2F_4CH_2CH_2)_2I$, **10a**, mp. 72–74 °C. ^1H NMR ($CDCl_3$) δ 2.36 (m, 4*H*), 2.68 (m, 2*H*), 3.24 (m, 2*H*). ^{19}F NMR ($CDCl_3$) δ −81.5 (tt, *J* = 10, 3 Hz, 3F), −115.3 (m, 2F), −115.7 (m, 4F), −124.7 (m, 2F), −126.4 (m, 2F).

*4.5. Preparation of 1,1,2,2,5,5,6,6-octahydroperfluoro-1-octanol, **11a** by oleum method*

A mixture of 1,1,2,2,5,5,6,6-octahydroperfluoro-1-iodooctane, **2a** (10.0 g) and oleum (15% SO_3, 20 mL) was heated to 60 °C for 1.5 h. A K_2SO_3 solution (1.5%, in ice–water 150 mL) was added to the reaction mixture while cooled with an ice–water bath. The resulting mixture was heated to 100 °C for 30 min. After being cooled to room temperature, a solid was precipitated. The liquid was decanted and the solid was dissolved in ether (200 mL) and washed with water (2 × 50 mL), saturated NaCl (50 mL), dried over anhydrous Na_2SO_4, concentrated and dried on vacuum to give a solid product, **11a** (7.0 g, yield, 96%, mp 48–49 °C). ^1H NMR ($CDCl_3$) δ 1.51 (t, 1*H*, *J* = 6 Hz, OH), 2.34 (m, 6*H*, CH_2), 2.47 (m, 2*H*, CH_2), 3.97 (dq, *J* = 6 Hz, *J* = 6 Hz, CH_2O). ^{19}F NMR ($CDCl_3$) δ −85.9 (bs, 3F, CF_3), −114.1 (m, 2F, CF_2), −116.0 (m, 2F, CF_2), −119.2 (m, 2F, CF_2).

*4.6. Preparation of 1,1,2,2,5,5,6,6-octahydroperfluoro-1-octanol, **11a** by NMF method*

A mixture of 1,1,2,2,5,5,6,6-octahydroperfluoro-1-iodooctane, **2a** (136.9 g) and *N*-methylformamide (NMF) (273 mL) was heated reaction to 150 °C for 19 h. The reaction mixture was washed with water (4 × 500 mL) to give a residue. A mixture of this residue, ethanol (200 mL), and concentrated hydrochloric acid (1 mL) was gently refluxed (85 °C bath temperature) for 2.5 h. The reaction mixture was washed with water (2 × 200 mL), diluted with dichloromethane (200 mL), dried over sodium sulfate overnight. The dichloromethane solution was concentrated and distilled at reduced pressure to give **11a** (60.8 g, yield 61%)

*4.7. Preparation of 1,1,2,2,5,5,6,6,9,9,10,10-dodecahydroperfluoro-1-dodecanol, **11b***

A mixture of 1,1,2,2,5,5,6,6,9,9,10,10-dodecahydroperfluoro-1-iodododecane, **2b** (65.6 g) and NMF (135 mL) was heated to 150 °C for 4 h. The reaction mixture was washed with water (~1 L) to give a solid product. This solid product was added ethanol (150 mL) and concentrated hydrochloric acid (1 mL) to the solids and heated at reflux (~85 °C) for 19 h. The reaction mixture was poured into water (500 mL) and the resulting solid was washed with water (3 × 300 mL), dried on vacuum to give **11b** (50.8 g, yield 98%, mp. 112–115 °C). ^1H NMR ($CDCl_3$) δ 1.52 (bs, 1*H*, OH), 2.34 (m, 10*H*, CH_2s), 3.97 (dq, *J* = 6 Hz, *J* = 6 Hz, CH_2O). ^{19}F NMR ($CDCl_3$) δ −85.9 (s, 3F, CF_3), −114.2 (m, 2F, CF_2), −115.8(m, 4F, CF_2s), −116.1 (m, 2F, CF_2), −119.2 (m, 2F, CF_2).

*4.8. Preparation of alcohol **12a** [$C_2F_5(C_2F_4CH_2CH_2)_2OH$] by oleum method*

A 250 mL flask was charged with $C_2F_5(C_2F_4CH_2CH_2)_2I$, **10a** (12 g) and oleum (15% SO_3, 125 mL) at room temperature. The resulting mixture was stirred at 60 °C for 2 h. A Na_2SO_3 solution (4 g in 100 mL) was added to the reaction mixture slowly at 60 °C bath between 65 and 90 °C internal temperatures. The resulting mixture was heated to 90 °C for 30 min. The liquid was decanted. The solid was dissolved in ether (150 mL) and washed with Na_2SO_3 (1 M, 20 mL), water (2 × 20 ml), NaCl (sat., 20 mL), dried over Na_2SO_4, concentrated and dried on vacuum to give a residue 9.5 g, which was further purified by distillation to give the alcohol, **12a**, 6.2 g, bp. 65–79 °C at 2 torr. ^1H NMR ($CDCl_3$) δ 1.58 (s, 1*H*), 2.36 (m, 6*H*), 3.97 (t, *J* = 7 Hz, 2H). ^{19}F NMR ($CDCl_3$) δ −81.5 (tt, *J* = 9.5, 3 Hz, 3F), −114.1 (m, 2F), −115.4 (m, 2F), −116.0 (m, 2F), −124.8 (m, 2F), −126.4 (m, 2F).

*4.9. Preparation of alcohol **13a** [$F(C_2F_4CH_2CH_2)_2SCN$]*

A mixture of the iodide **2a** (8.9 g), KSCN (2.5 g) and acetone (30 mL) was refluxed for 5 h. After being cooled to room temperature, the reaction mixture was poured into water (200 mL). The solid was collected by filtration and washed with water (2 × 40 mL), dried on vacuum to give **13a** (a white solid, 7.1 g, 96% yield). MS (m/e) 333 (M+, 100%), 255 (24%), 235 (30%), 306 (11%), 197 (49%), 177 (91%), 77 (92%). ^1H NMR ($CDCl_3$) δ 2.28 (m, 4*H*), 2.55 (m, 2*H*), 3.10 (m, 2*H*). ^{19}F NMR δ −85.9 (s, 3F), −114.7 (m, 2F), −115.4 (m, 2F), −119.2 (t, *J* = 17 Hz, 2F).

*4.10. Synthesis of azide **14** [$F(CF_2CF_2CH_2CH_2)_nN_3$]*

Crude ETFE cotelomer iodides **2** [$F(CF_2CF_2CH_2)_nI$, wherein $n = 2$, 3 were major components in about 2:1 ratio] (10.0 g) was added to a solution of sodium azide (2.03 g) in acetonitrile (90 mL) and water (34 mL). The mixture was allowed to heat at 90 °C until the reaction was determined complete by gas chromatography. By 36 h, complete conversion of the iodides to azides was observed. The mixture was cooled to room temperature and the bulk of the acetonitrile evaporated under vacuum. The resulting slurry was extracted with methylene chloride (3 × 60 mL). The organic layer washed with water (2 × 80 mL), brine (1 × 80 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent and vacuum drying provided the cotelomer azides **14** $[F(CF_2CF_2CH_2CH_2)_nN_3]$ as a white solid (6.0 g). GC–MS: 2 major peaks correspond to $n = 2$ and n = 3 azides in about 2:1 ratio: ^1H NMR ($CDCl_3$): δ 3.52 (bt, $J = 6.0$ Hz, N–CH_2), 2.29 (bm, CF_2–CH_2's).

4.11. Synthesis of amine ***15*** *$[F(CF_2CF_2CH_2CH_2)_nNH_2]$*

An ETFE cotelomer azide mixture **14** $[F(CF_2CF_2CH_2CH_2)N_3$, wherein $n = 2$, 3 were major components in about 2:1 ratio] (2.25 g), and Ni-Raney (0.032 g) was added to a solution ethanol (5 mL) and water (5 mL). To the stirring mixture was slowly added hydrazine hydrate (0.328 g). After the addition was complete, the mixture was progressively heated to 60 °C and stirred at 60 °C for 12 h. The reaction mixture was cooled to room temperature and methylene chloride (30 mL) was added and stirred for 10 min. The resulting mixture was filtered and washed with water (2 × 20 mL) and brine (1 × 20 mL). Evaporation of the solvent followed by recrystallization from methylene chloride/hexane provided the amine **15** $[F(CF_2CF_2CH_2CH_2)_nNH_2]$ as a light brown solid (1.9 g). GC: 2 major peaks correspond to $n = 2$ and $n = 3$ amines (about 2:1 ratio). ^1H NMR ($CDCl_3$): δ 3.05 (bt, $J = 6.0$ Hz, NH_2–CH_2), 2.29 (bm, CF_2–CH_2's).

4.12. Synthesis of thiol ***16*** *$F(CF_2CF_2CH_2CH_2)_nSH$*

Crude ETFE cotelomer iodides **2** $[F(CF_2CF_2CH_2CH_2)_nI$, wherein $n = 2,3$ were major components in about 2:1 ratio] (10.0 g) were added to a solution of thiourea (2.03 g) in absolute ethanol (100 mL) kept at 70 °C. The mixture was continued to heat at 80 °C until the reaction was determined complete by the disappearance of iodide by gas chromatography. By 36 h, 98% consumption of the iodide was observed. The mixture was concentrated and treated with a solution of sodium hydroxide (1.92 g) in water (5 mL). The mixture was stirred overnight at ambient temperature and then heated to boiling for 30 min. The reaction mixture was then cooled to ambient temperature and 5% sulfuric acid was added drop wise until solution was acidic. The mixture was then extracted with methylene chloride (3 × 50 mL), the organic layer dried over anhydrous $MgSO_4$ and evaporated to obtain the cotelomeric thiols **16** $[F(CF_2CF_2CH_2CH_2)_nSH]$ as a white solid (5.8 g). GC–MS: 2 major peaks corresponded to $n = 2$ [(m/e) 308] and $n = 3$ thiols [(m/e) 436] in about 2:1 ratio. ^1H NMR (CDCl3): δ 2.79 (bt, $J = 6.0$ Hz, S–CH_2), 2.32 (bm, CF_2–CH_2's)

4.13. Synthesis of hydroxyethyl sulfide ***17*** *$F(CF_2CF_2CH_2CH_2)_nSCH_2CH_2OH$*

To a solution of 2-mercaptoethanol (1.41 g) and sodium hydroxide (0.720 g) in *tert*-butanol (10 mL) heated to 80 °C, was slowly added to crude ETFE cotelomer iodides **2** $[F(CF_2CF_2CH_2CH_2)_n$ (wherein $n = 2,3$ were major components in about 2:1 ratio] (5 g). The mixture was allowed to heat at 80 °C for 12 h and the reaction was determined complete by gas chromatography. The mixture was cooled to ambient temperature and the precipitated product was filtered and washed repeatedly with cold water followed by a mixture of 1:1 methylene chloride and hexane. The product was dried under vacuum to obtain the cotelomeric alcohol $F(CF_2CF_2CH_2CH_2)_nSCH_2CH_2OH$ (**17**) as a white solid (3.4 g) .GC–MS: 2 major peaks corresponded to $n = 2$ [(m/e) 352] and $n = 3$ alcohols [(m/e) 480] in about 2:1 ratio. ^1H NMR ($CDCl_3$): δ 3.40 (t, $J = 6.8$ Hz, OCH_2), 2.81 (t, $J = 6.8$ Hz, SCH_2), 2.79 (m, SCH_2), 2.35 (bm, CF_2CH_2's).

4.14. Synthesis of aminoethyl sulfide ***18*** *$[F(CF_2CF_2CH_2CH_2)_nSCH_2CH_2NH_2]$*

To a solution of 2-aminoethanethiol (1.39 g) and sodium hydroxide (0.720 g) in *tert*-butanol (10 mL) heated to 80 °C was slowly added to crude ETFE cotelomer iodide **2** $[F(CF_2CF_2CH_2CH_2)_nI$ wherein $n = 2,3$ were major components in about 2:1 ratio] (5 g), The mixture was allowed to heat at 80 °C for 12 h and the reaction was determined complete by gas chromatography. The mixture was cooled to ambient temperature and the precipitated product was filtered and washed repeatedly with cold water followed by a mixture of 1:1 methylene chloride and hexane. The white solid was dried under vacuum to obtain the ether amines **18**, $[F(CF_2CF_2CH_2CH_2)_nSCH_2CH_2NH_2]$ as a mixture of cotelomers (3.9 g). GC–MS: 2 major peaks corresponded to $n = 2$ [(m/e) 351] and $n = 3$ amines [(m/e) 479] in about 2:1 ratio. ^1H NMR ($CDCl_3$): δ 3.04 (t, $J = 6.0$ Hz, NCH_2), 2.79 (t, $J = 6.6$ Hz, SCH_2), 2.76 (t, $J = 6.6$ Hz, SCH_2), 2.37 (bm, CF_2CH_2's).

4.15. Crystallography

X-ray data for **2a** were collected at −100 °C using a Bruker 1K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator. The structures were solved and refined using the Shelxtl software package, [39] refinement by full-matrix least squares on F2, scattering factors from Int. Tab. Vol. C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #1010680. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk).

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