Methyl-Terminated Perfluoroalkyl Iodides and Related Compounds

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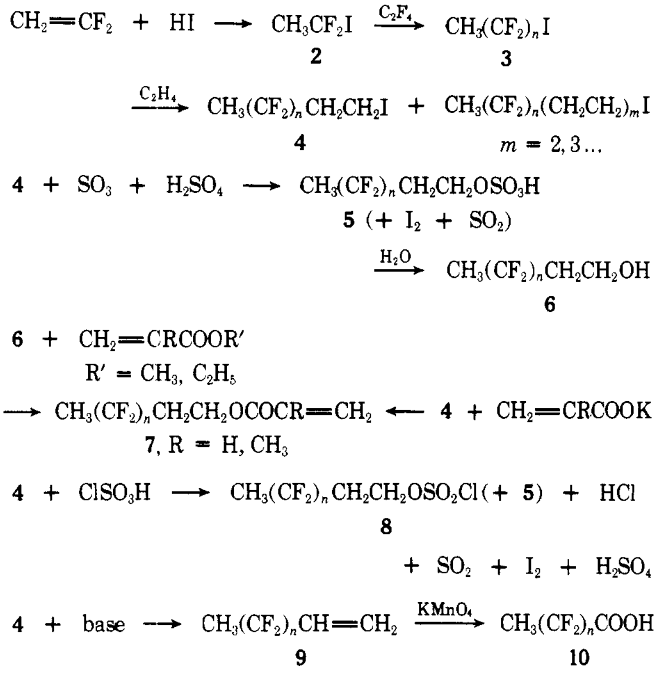
1,1-Difluoroethyl iodide (**2**) was prepared from vinylidene fluoride and hydrogen iodide in 96% yield. It telomerized with tetrafluoroethylene with acyl peroxide catalysis, but other radical generators were ineffective. The telomers $CH_3(CF_2)_nI$ (**3**) reacted thermally with ethylene to form $CH_3(CF_2)_nCH_2CH_2I$ (**4**). These in turn were converted to alcohols (**6**), (meth)acrylates (**7**), and chlorosulfates (**8**) by replacement of the iodine atom. The radical $CH_3(CF_2)_n\cdot$, when formed during telomerization of **2** with tetrafluoroethylene or during reaction of **3** with ethylene, may lose CF_2 groups successively, since products derived from $CH_3(CF_2)_{n-y}$ (y = 1, 2, 3) were always identified in the reaction mixtures. The presumed difluoromethylene fragment is held responsible for some of the other trace by-products. $CH_3CH_2CF_2CF_2I$ was prepared from $ICH_2CH_2CF_2CF_2I$.

Polymers derived from 2-perfluoroalkylethyl (meth)acrylates $CF_3(CF_2)_nCH_2CH_2OCOCR{=}CH_2$ (**1**) are useful in treating the surfaces of textiles and other substrates. Since theoretical analysis[1] suggested that similar compounds with a terminal methyl group might exhibit valuable surface properties, the compounds **7** (Chart I) were prepared for evaluation. Telomerization of 1,1-difluoroethyl iodide (**2**) with tetrafluoroethylene (TFE) was employed for synthesis of the intermediates (eq 1).

Chart I



$$CH_2{=}CF_2 + HI \longrightarrow \underset{\mathbf{2}}{CH_3CF_2I} \xrightarrow{C_2F_4} \underset{\mathbf{3}}{CH_3(CF_2)_nI}$$

$$\xrightarrow{C_2H_4} \underset{\mathbf{4}}{CH_3(CF_2)_nCH_2CH_2I} + \underset{m\,=\,2,3\ldots}{CH_3(CF_2)_n(CH_2CH_2)_mI}$$

$$\mathbf{4} + SO_3 + H_2SO_4 \longrightarrow \underset{\mathbf{5}\ (+\ I_2\ +\ SO_2)}{CH_3(CF_2)_nCH_2CH_2OSO_3H} \xrightarrow{H_2O} \underset{\mathbf{6}}{CH_3(CF_2)_nCH_2CH_2OH}$$

$$\mathbf{6} + \underset{R' = CH_3,\ C_2H_5}{CH_2{=}CRCOOR'} \longrightarrow \underset{\mathbf{7},\ R\ =\ H,\ CH_3}{CH_3(CF_2)_nCH_2CH_2OCOCR{=}CH_2} \longleftarrow \mathbf{4} + CH_2{=}CRCOOK$$

$$\mathbf{4} + ClSO_3H \longrightarrow \underset{\mathbf{8}}{CH_3(CF_2)_nCH_2CH_2OSO_2Cl} (+\ \mathbf{5}) + HCl + SO_2 + I_2 + H_2SO_4$$

$$\mathbf{4} + \text{base} \longrightarrow \underset{\mathbf{9}}{CH_3(CF_2)_nCH{=}CH_2} \xrightarrow{KMnO_4} \underset{\mathbf{10}}{CH_3(CF_2)_nCOOH}$$

$$\underset{\mathbf{2}}{CH_3CF_2I} + xC_2F_4 \xrightarrow{\text{radical}} \underset{\mathbf{3}}{CH_3CF_2(CF_2CF_2)_xI} \qquad (1)$$

The required telogen **2** had already been prepared by iodine-catalyzed addition of hydrogen iodide to vinylidene fluoride (1,1-difluoroethane); on a small scale, the reaction was slow.[2] Actually, the reaction is very rapid and exothermic as soon as sufficient product has been formed to act as a mutual solvent for vinylidene fluoride and hydrogen iodide. Added iodine may not be really essential; the traces of iodine present in commercial hydrogen iodide are probably quite sufficient, if in fact necessary. The reaction can be conducted as quickly as the available cooling permits. Pure **2** was obtained in 96% yield.

Telomerization. Many literature methods for telomerization of *per*fluoroalkyl iodides with TFE failed with **2**. Perfluorobutyl iodide difluoride ($C_4F_9IF_2$)[3] reacted violently with **2** at room temperature to yield iodine; this mixture did not react with TFE. The ultraviolet light passed by Pyrex glass did not cause telomerizations at temperatures to 80 °C and TFE pressures to 200 psi. Azonitriles such as 1,1′-azobis(cyclohexanecarbonitrile) were ineffective. Di-*tert*-butyl peroxide likewise gave no telomer at temperatures to 135 °C where the peroxide decomposes fairly rapidly to *tert*-butoxy radicals. This peroxide was not tested with **2** at 160 °C where the *tert*-butoxy radical dissociates to methyl radical and acetone; pentafluoroethyl iodide will telomerize with TFE under these conditions, but not at 130 °C. Methyl amyl ketone peroxide at 80 °C failed to initiate telomerization; it is frequently used in other telomerizations with TFE. *tert*-Butyl hydroperoxide with cobaltous ion promoter was initially effective, but the reaction slowed to a halt as insoluble cobaltous iodide precipitated.

Thermal telomerization (no catalyst) occurred at 200 °C, analogous to the thermal telomerization of *per*fluoroalkyl iodides with TFE. However, the vapor pressure of the telogen **2** is nearly equal to the cylinder pressure of TFE, and it was impractical to add TFE continuously to achieve reasonable conversions. On the other hand, when the higher telogen $CH_3CF_2CF_2CF_2I$ had become available (see below), its lower vapor pressure permitted continuous feed to achieve TFE conversions of 0.7 mol/mol of telogen.

Fortunately, *acyl* peroxides are very effective. Benzoyl peroxide was tested first, despite its penchant for undergoing induced decompositions,[4] and telomerization occurred readily. However, the iodobenzene by-product boils too close to the telomer **3**, n = 7, for efficient separation. Other by-products included $C_6H_5CF_2CH_3$ and its isomeric ring-iodinated derivatives, and iodobenzoic acids. Hence other commercially available peroxy acid derivatives were screened. The search culminated with the demonstration that *tert*-butyl peroxypivalate ("Lupersol" 11) was extraordinarily effective, even at 0.04 mol % concentration. It appears that alkoxy radicals $RO\cdot$ are inefficient in abstracting iodine from R_FI, since a high-energy hypoiodite ROI would be the product. On the other hand, carbon radicals $R\cdot$ from decomposition of acyloxy radicals $RCOO\cdot$ or *tert*-butoxy radicals would form RI, and that abstraction should be nearly thermoneutral.

Telomerizations were performed by feeding TFE continuously to the telogen–catalyst mixture at 50 °C, 120–160 psi, at such a rate that the temperature did not rise. In the small apparatus described in the Experimental Section, a cooling coil permitted rapid addition. Usually 0.5 mol of TFE was added per mol of telogen so as to maximize the quantities of the desired telomers n = 5–11. Larger amounts of TFE increased the quantities of higher telomers, $n > 11$. The individual telomers were isolated by fractional distillation.

Curiously, the expected telomers **3** (n = odd integer) were accompanied by small amounts of products with n = an even integer. The TFE used was free of hexafluoropropene; the by-product did not possess a trifluoromethyl group $-CF_2CF(CF_3)-$ (NMR). The only explanation apparent at this writing is that the growing radical $CH_3(CF_2)_n\cdot$ lost the elements of CF_2 (difluoromethylene) to give $CH_3(CF_2)_{n-1}\cdot$. Other trace products found in the crude telomer product may have been derived by insertion of the lost difluoromethylene into C–H bonds (see Experimental Section).

Ethylene Insertion. The pure individual telomers **3** were heated at 195 °C under 200–250 psi ethylene pressure. Only small amounts of ethylene telomers $CH_3(CF_2)_n(CH_2CH_2)_mI$ accompanied the major product **4**. The hydrocarbon radical $RCH_2\cdot$ is much more reactive toward chain transfer with R_FI than is the fluorocarbon radical $R_F\cdot$; hence most ethylene adduct radicals are destroyed by chain transfer before they can add more ethylene. Moreover, a telogen **3** is readily reinitiated, but product **4** is not. Independent experiments showed that neither **4** nor the related $R_FCH_2CH_2I$ reacted significantly with ethylene at 200 °C. See also the attempted telomerizations of TFE with ethyl iodide below.

In these reactions also, a few of the intermediate radicals $CH_3(CF_2)_n\cdot$ lost difluoromethylene groups, since the compounds $CH_3(CF_2)_{n-y}CH_2CH_2I$ (y = 1, 2, 3) were detected by GC/MS. The unreacted **3** also contained lower homologues not present originally. Traces of products derivable from ICF_2CF_2I and ethylene were detected as well (see below).

Hydrolysis of 4 to Alcohols 6. Basic hydrolysis of the iodides **4** causes chiefly elimination to olefins **9** (see following section).[5] Hence **4** were hydrolyzed by oleum and hot 30% sulfuric acids to **6**. Hydrolysis of the chlorosulfates **8** yielded a mixture of products.

Preparation of (Meth)acrylates 7 (see Chart I). Some of the iodides **4** were transformed to esters by heating them with potassium (meth)acrylate in dry *tert*-butyl alcohol. Although the yields were acceptable, the reaction was slow and always gave some of the olefin as by-product. Preferably, alcohols **6** were transesterified with methyl methacrylate or ethyl acrylate, using tetraisopropyl titanate as ester interchange catalyst. Yields by the second procedure were nearly quantitative, and no olefin was formed.

The (meth)acrylates formed by either procedure polymerized readily with conventional initiators in bulk, in solution, or in emulsion.[6]

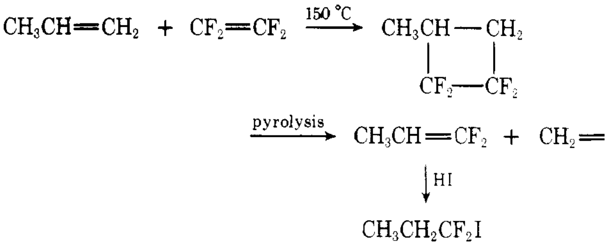
Preparation of Olefins 9. Some of the olefins were isolated from the potassium methacrylate displacements. Others were prepared by refluxing the iodide **4** with ethanolic potassium hydroxide. Heating **4** with pyridine gave slow and incomplete elimination. One of the olefins (n = 9) was oxidized to the acid **10** with potassium permanganate.

Reaction of Iodides 4 with Chlorosulfonic Acid. When the iodides **4** were heated with chlorosulfonic acid, the chlorosulfates **8** were the major products. Most of the remainder was alkylsulfuric acid **5**, but a small amount of the related chloride $CH_3(CF_2)_nCH_2CH_2Cl$ was also formed. The chlorosulfates were identified by elemental analysis, NMR, and IR.

Curiously, the mass spectra were anomalous. The compounds **8**, n = 3 (or 5), should exhibit a pair of peaks for *m/e* 308, 310 (or 408, 410) (chlorine isotopes). Yet these peaks were not observed. Rather, the most abundant peak was *m/e* 303 (or 403), with minor peaks at *m/e* 304, 305, and 307 (or 404, 405, and 407). Even more curiously, the higher homologue **8**, n = 7, gave the expected peaks at *m/e* 508, 510 and none of the *m/e* 503 or other anomalous peaks. No explanation is apparent for these peculiar results.

Synthesis of $CH_3CH_2CF_2CF_2I$ (15). The iodide **15** was sought as the starting point for preparation of similar derivatives. A priori, the most attractive synthesis would be telomerization of ethyl iodide with TFE. Bartlett and Nozaki[4] have shown that benzoyl peroxide undergoes induced decomposition in ethyl iodide, presumably because ethyl radicals are formed. However, ethyl iodide is a much poorer chain-transfer agent than perfluoroethyl iodide or other R_FI; hence one would expect that a growing radical $C_2H_5(CF_2CF_2)_n\cdot$ should more readily add to TFE than transfer with ethyl iodide. Unfortunately, this prediction was borne out. When ethyl iodide containing benzoyl peroxide was heated at 80 °C under 120 psi pressure of TFE, the product was a fine dispersion of polymer in ethyl iodide. Iodobenzene and carbon dioxide were formed, but no GC peaks corresponding to the low telomers were seen. With *tert*-butyl peroxide at 135 °C (half-life 3.86 h), the product was a clear, greenish liquid with a white, fluffy solid. The liquid phase contained only traces of low telomer.

A second route was examined (eq 2). Two experiments



(2)

showed that the first step proceeded in only about 50% yield based on TFE. Since the pyrolysis gives only moderate yields, this route was not further pursued. It is unfortunate that 2-butene fails to undergo cycloaddition with TFE.[7,8]

Finally, the route shown in Chart II was developed with

Chart II

$$C_2F_4 + I_2 \longrightarrow \underset{\mathbf{11}}{ICF_2CF_2I} \xrightarrow{C_2H_4} \underset{\mathbf{12}}{ICH_2CH_2CF_2CF_2I} + ICH_2CH_2CF_2CF_2CH_2CH_2I$$

$$\mathbf{12} + NaBH_4 \longrightarrow \underset{\mathbf{13}}{ICH_2CH_2CF_2CF_2H}$$

$$\mathbf{12} + Et_3N \longrightarrow \underset{\mathbf{14}}{CH_2{=}CHCF_2CF_2I} \xrightarrow{N_2H_2} CH_3CH_2CF_2CF_2I$$

moderate success. Since the diiodide **12** was readily prepared,[9] the problem was reduced to finding a method for selectively hydrodeiodinating CH_2I in the presence of CF_2I. Chromous sulfate–ethanolamine in dimethylformamide[10] furnished only a small amount of low-boiling products, a complex mixture containing only a trace of **15** (GC/MS); most of the **12** was recovered. Sodium borohydride in methanol reduced **12** slowly to **13** in about 65% yield (GC). **13** was identified by NMR and GC/MS. Though potentially a useful method for converting R_FI to R_FH,[11] borohydride reduction could not be employed in the synthesis of **15**. Apparently neither one-electron nor two-electron reducing agents attack R_HI in preference to R_FI.

Heating **12** with excess triethylamine in *tert*-butyl alcohol eliminated hydrogen iodide slowly to form the olefin **14** in about 50% yield.[12] Potassium hydroxide in isopropyl alcohol effected some elimination, but much of material was converted either to water-soluble or gaseous products. The olefin was then reduced to **15** with diimide[13] generated from hydrazine–hydrogen peroxide with cuprous chloride catalysts. Sufficient **15** was obtained to permit identification, but not enough to study its telomerization, etc. This two-step route from **12**, with more study, could become a satisfactory source of **15**.

Experimental Section

Apparatus. Small-scale experiments under pressure were conducted in graduated heavy-wall Pyrex tubes or bottles (respectively 3 and 6 oz capacity) purchased from the Fischer-Porter Co. under the name "aerosol compatibility tubes". These are closed with metal connectors equipped with replaceable Viton fluoroelastomer O-rings. The basic assembly is pictured in the F-P catalog. The connector for the reaction bottle was drilled to accommodate a cooling coil, a thermocouple well, and a valved sampling tube (dip-leg) fashioned from 0.125 in. Monel tubing; these were welded to that connector. An adapter (0.125 in pipe to 0.25 in. tube) screwed into the connector was attached to a cross. One arm of the cross was connected through a tee to a 30 in.–300 psi gauge and to a ball-valved vent line leading to the top of the hood. The second arm of the cross led through a needle valve to the vacuum manifold. The third arm led to the interconnection described below.

Gases were condensed and measured in a similar tube lacking the dip-leg and cooling coil. It was similarly furnished with a gauge and vent, and attached to the vacuum manifold adjacent to the reaction bottle. The reaction bottle and gas tube were interconnected through the third arms of the crosses to a solenoid-operated valve. A tube led from this interconnection to a Mon-O-Con pressure gauge equipped with adjustable contacts. The output from this gauge opened or closed the solenoid valve as the pressure fell or rose between the upper and lower set points. The solenoid valve was protected by a ball valve between it and the reaction bottle.

The vacuum manifold was 1 in. (i.d.) Monel pipe. A 1-in. ball valve led to a conventional trapped pumping system. Valved ports led to trapped pressure gauges and to connectors for gas cylinders. All permanent connections were assembled by Heliarc welding; temporary connections were made with Swagelok connectors. All but the solenoid valves were Whitey needle or ball valves (0.25 in.). All tubing was 0.25 in., except as noted. Monel metal was used throughout to minimize corrosion.

The cooling coil in the reaction bottle carried laboratory water through a throttling needle valve and a solenoid-operated valve (Hoke). A Simplytrol controller attached to the thermocouple provided the signals to open and close the water valve to maintain an exothermic reaction at constant temperature. The glassware was dried at 200 °C for 24 h before use.

Gaseous reagents were transferred from cylinders through the vacuum manifold and condensed in evacuated tubes at −196 °C, then warmed to −80 °C for measurement. Vinylidene fluoride was used from cylinders as supplied (Matheson). Tetrafluoroethylene was stored outdoors and delivered from the cylinder at 30 psi through a copper line past a mineral oil bubbler and a silica gel tower (to remove the limonene inhibitor) into the vacuum manifold. Uninhibited TFE must never be stored because of the danger of explosive polymerization or disproportionation. The temperature of the condensed gas was then adjusted with an appropriate bath to yield the desired vapor pressure.

In operation, any involatile reagents were placed in the reaction bottle with a magnetic stirrer bar. The bottle was attached to the connector, chilled to a temperature at which the contents had negligible vapor pressure, and evacuated. Note: the cooling coil must not contain water from a previous experiment; it may be conveniently flushed out with methanol and dried with air. Where desirable, liquids were degassed by successive freeze–thaw cycles. The temperature of the reaction bottle was then adjusted with an appropriate bath. For temperatures above about 50 °C, an electric cooking pot with thermostatic control, filled with water or peanut oil, was a very convenient constant-temperature bath. The gaseous reagent was then added through the interconnection at the selected constant pressure.

In over 100 experiments with this apparatus, no bottle breakage or other accidents occurred. However, the experimenter must realize that pressure reactions in glass are hazardous. Care is required to avoid scratching the glass bottles. In all our work, sturdy shields of 0.5 in. Lucite abrasion-resistant sheet guarded all the glass equipment, including the faces of the gauges. A further safety note: the violent and exothermic decomposition of TFE under pressure may be initiated by traces of oxygen; good vacuum-line technique is required at all times.

The apparatus and technique described permitted reactions up to about 90 °C and 200 psi, and could make about 190 mL of total product. For higher temperatures and pressures, 400-mL shaker tubes of Hastelloy C were used in a laboratory specially equipped for high-pressure research. The large preparations of 1,1-difluoroethyl iodide were conducted in a 2-gal stirred autoclave of Hastelloy B equipped with a cooling coil.

1,1-Difluoroethyl Iodide. Several exploratory experiments were conducted in the apparatus described. A little iodine was placed in the bottle, and hydrogen iodide was transferred in from a cylinder (Matheson). A new cylinder contained enough hydrogen or other noncondensible gas to impede the transfer, but it was readily removed by pumping out the manifold several times (liquid nitrogen trap!). The problem did not recur during subsequent uses of that cylinder. Note the narrow liquid range of hydrogen iodide [mp −51 °C, bp −35 °C (760 Torr)]. Alternatively, and more conveniently with larger runs, the cylinder was chilled to about −30 °C and liquid hydrogen iodide was poured from the cylinder through a copper coil into the bottle at −80 °C; the exit side was protected by −80 °C traps. The bottle was then weighed, connected to the vacuum manifold, and evacuated while at −196 °C.

The hydrogen iodide was then brought to −20 °C, and vinylidene fluoride (previously condensed and measured in the gas tube described) was admitted to 150 psi. The reaction was very sluggish at first, but as product formed, it became faster and more exothermic. After about one-third of the vinylidene fluoride had been added, an ice bath was required to maintain the temperature at 40–45 °C. Cooling water was also fed through the coil, and the automatic feed valve was set for 150 psi. After 1 mol of vinylidene fluoride had reacted, the reaction stopped abruptly. The mixture was held for 0.5 h at 40–45 °C, 150 psi, to ensure complete consumption of the hydrogen iodide. The mixture was then cooled to 0 °C and vented through −80 °C traps to remove the excess vinylidene fluoride.

The trap contents and the main product were combined and washed at −10 °C with cold brine containing sodium bisulfite to reduce the iodine. It was then washed with ice water and dried with calcium chloride before distillation. It boiled very constantly at 45 °C. The yield in several experiments was 95% when stringent precautions were taken to prevent evaporative losses. The still residue, about 0.3% of the product, showed a GC trace suggestive of telomers of vinylidene fluoride with **2**, probably $CH_3CF_2(CH_2CF_2)_xI$, and 1,1-difluoro-1,2-diiodoethane from addition of iodine to vinylidene fluoride.

A large run[14] was made in the 2-gal autoclave, to which had been added 10 g of iodine. It was cooled to −40 °C and evacuated, and 5067 g of hydrogen iodide was added liquid phase from chilled cylinders. The vent from the autoclave was connected to two −80 °C traps in series, the contents of which were added to the autoclave at the end of the addition. The weight was determined from the loss in weight of the cylinders. Vinylidene fluoride was then added vapor phase from a tared cylinder to a pressure of about 150 psi, and the mixture was then warmed to 30 °C. When the reaction became exothermic, it was controlled by circulating chilled acetone from an external −80 °C bath through the internal cooling coils. When 2740 g had been added, the reaction stopped; about 2.5 h was required. The mixture was held for 0.5 h longer, then chilled to −40 °C. The autoclave was vented through a −80 °C condenser delivering into a chilled 12-L flask, and the product was poured into that flask and allowed to warm to room temperature under the −80 °C condenser. The product was then fractionated. The yield of constant-boiling **2** was 96%.

Telomerization of 2 with Tetrafluoroethylene. All of the exploratory work was done in the glass pressure bottles. The catalyst to be tested and the telogen were added to the reaction bottle, which was then attached to the vacuum manifold, chilled first to −80 °C, then to −196 °C, and evacuated. (Although we occasionally cooled directly from room temperature to −196 °C, or warmed from −196 °C to room temperature with a methanol bath, and never had a tube crack, safe practice dictates performing the heating or cooling in two steps.) The contents were then brought to the desired reaction temperature. Meanwhile, TFE was condensed in an evacuated tube and measured at −80 °C. It was then warmed to the desired pressure with an appropriate bath and fed to the reaction mixture as described above. Further details are given below. When the reaction was judged complete, the mixture was cooled to −20 °C, and the unreacted TFE was stripped out by vacuum transfer into a calibrated tube for measurement.[15] It was then discarded. Usually 0.5–0.7 mol of TFE was fed per mol of telogen.

The product was then transferred to distillation equipment and the unreacted telogen was removed at atmospheric pressure through a fractionating column packed with $^3/_{16}$ in. protruded stainless steel packing. The residue was then fractionated in vacuo.

No more will be said about the unsuccessful experiments mentioned in the Discussion section. Telomerization with benzoyl peroxide required at least 1 mol % of this initiator to achieve conversion of 0.5 mol of TFE per mol of **2** at 80 °C, 200 psi, ending at 90–95 °C, 275 psi. Smooth reaction occurred when the stirring was efficient. Several good

Table I. Properties of Telomers $CH_3(CF_2)_nI$, 3[a]

n	Bp, °C (Torr)	Mp, °C	Formula
1[b]	45.6 (760)		
3	95.0 (760)		$C_4H_3F_6I$
5	93 (172)		$C_6H_3F_{10}I$
7	94 (53)		$C_8H_3F_{14}I$
9	118 (38)	50	$C_{10}H_3F_{18}I$
11	125 (17)	79–80	$C_{12}H_3F_{22}I$
13[c]	155 (21)	113–114	$C_{14}H_3F_{26}I$
15	166 (15)[d]		

[a] Satisfactory values for microanalysis for C and H, and in most cases F and I, were obtained for these compounds. NMR spectra in CCl_3F and mass spectra were consistent with the structures. In addition, the homologues *n* = 2, 4, 6, and 8 were identified by GC/MS. [b] Known compound, ref 1. [c] The compounds *n* = 13 and 15 could not be separated completely by distillation or crystallization. [d] Not obtained pure.

Table II. Properties of Telomers $CH_3(CF_2)_nCH_2CH_2I$, 4[a]

n[b]	Bp, °C (Torr)	Mp, °C	Formula
3	101.3 (96)[c]		$C_6H_7F_6I$
5	114 (50)		$C_8H_7F_{10}I$
7	109 (10)	40.0–40.5	$C_{10}H_7F_{14}I$
9	131 (10)	70.0–70.5	$C_{12}H_7F_{18}I$
11	155 (12)	94–95	$C_{14}H_7F_{22}I$
13		122.0–122.5[d]	$C_{16}H_7F_{26}I$
15		133–134[e]	

[a] Satisfactory microanalyses for C, H, and I, and in some cases F, were obtained for these compounds. NMR spectra in CCl_3F and mass spectra were consistent with the structures assigned. [b] Some of the compounds *n* = 1, 2, 4, 6, and 8 were identified by GC/MS. [c] Also bp 164 °C (760 Torr); at this temperature, the iodide attacks the stainless steel packing. [d] Recrystallized from acetone. [e] Since the starting iodide was not pure, this product was a mixture of roughly equal amounts of *n* = 13 and 15.

runs were combined for fractional distillation. The progress of the fractionation was followed by GC analysis (see below). Intermediate cuts were redistilled to concentrate the impurities. GC/MS permitted identification of the following impurities: C_6H_5I, an iodobenzoic acid, an isomer of $IC_6H_4CF_2CH_3$ (action of $CH_3CF_2\cdot$ on iodobenzene), $H(CF_2)_5F$, $H(CF_2)_6F$, $CF_3CF_2CHFCF_2I$, $ICH_2CF_2CF_2I$, $ICF_2CF_2CH_2(CF_2)_3I$, and the telomer series with an *even* number of CF_2 groups mentioned in the Discussion section. Formation of most of these compounds obviously requires hydrogen abstraction by a growing radical, in some cases followed by iodine transfer. Since these compounds (except for iodobenzene) are formed in only trace amounts, hydrogen abstraction is not an important side reaction in this telomerization.

Thermal telomerization (no catalyst) with **2** was conducted at 195 °C in a 400-mL shaker tube.[16] Since no compressor for TFE was available, and since the vapor pressure of **2** at the reaction temperature was almost equal to the cylinder pressure of TFE, it was difficult to achieve significant conversion. Although telomers were formed (GC), thermal telomerization was not pursued when a superior method was found.

Exploratory experiments with *tert*-butyl peroxypivalate (Lupersol 11, supplied by Lucidol Co. as a 75% solution in mineral spirits) were conducted in glass as described. But safety considerations prohibited use of a large autoclave with TFE. Accordingly, 31 telomerizations were conducted by the following general procedure. The 400-mL shaker tube was chilled to −80 °C, and 580 g (chilled) of **2** was poured in. The catalyst was then added. In early runs, 5 g was used. Later the amount was reduced until the last 12 runs were made with only 0.3 g of this material (corresponding to 0.04 mol %). The bomb was sealed, weighed, pressure tested, and evacuated at −80 °C. Then 15 g of uninhibited TFE was added from a tared small cylinder on a balance. It was then heated to 50 °C; the pressure was 120–180 psi. Too rapid feed of TFE will cause a sudden exothermic reaction, with destruction of the catalyst, or worse. Near the end, the pressure was raised to 300 psi, the temperature to 70 °C. The total TFE fed was 160 g. The bomb was then reweighed, cooled to −80 °C, vented, and discharged into a cold bottle for refrigerated storage.

Several runs were combined and warmed to room temperature under a −80 °C condenser to separate dissolved TFE. Unreacted telogen was distilled out through a 1-m fractionating column fitted with protruded packing; it was 99.9% pure (GC) and was suitable for recycle. The telomers were separated by fractional distillation at reduced pressure (Table I).

In one such group, the following results were obtained. From a total of 10.905 kg of **2**, 57.0 mol, and 3.568 kg of TFE fed, 35.7 mol, 0.627 mol/mol (by weight gain), 5.638 kg of telomers **3**, *n* ≥ 3, was obtained. Its composition on a weight basis was 34.6, 22.4, 17.4, 12.6, 7.1, and 6.0%, on a mole basis 47.5, 23.0, 14.2, 8.6, 4.0, and 2.7% for the respective telomers *n* = 3, 5, 7, 9, 11, and ≥13. Thus 0.518 mol of TFE (average) per mol of telogen was actually incorporated into products.

All the telomers **3** up to *n* = 11 were obtained pure. The telomer *n* = 13 was obtained in only 95% purity (contaminated by *n* = 15). The higher telomers decomposed at pot temperatures above 170–180 °C, and the telomer *n* = 13 melted at 113 °C. A specially designed column and thermostated stillhead would have permitted separation of pure telomers *n* = 13 and 15.

Telomerization of the telomer **3**, *n* = 3, with Lupersol 11 by the above procedure was facile, and the product distribution was somewhat "sharper", i.e., the amounts of higher telomers fell off more rapidly, than with the telogen **2**. "Thermal" telomerizations were performed without catalyst at 200 °C; the vapor pressure of this telogen was low enough (120 psi) to permit easy TFE feed. From a total of 2012 g (6.88 mol) of telogen and 532 g of TFE (mole ratio 0.723), 2532 g of product was obtained. Fractionation yielded, in addition to recovered telogen, 640 g, 46%; 307 g, 22%; 454 g, 32%; of the respective telomers *n* = 5, 7, and ≥9.[17] The product distribution was again sharper than with **2** because CH_3CF_2I transfers iodine less readily than does $CH_3(CF_2)_3I$.[11]

Analysis. GC analysis of the mixtures encountered in this work was conducted on DC-200 silicone oil (20% on Chromosorb P, 45–60 mesh), with helium as carrier gas, TC detector. Solid products were dissolved in trichlorotrifluoroethane (Freon 113) before injection. Areas were determined by triangulation; calibration factors were applied to give weight percent. To identify trace components, the desired peaks were trapped, then injected into a mass spectrometer. Identification was made by comparison to our extensive library of mass spectra of fluorocarbons. In some cases, structures were inferred from the molecular ion peak and the cracking pattern. I am indebted to Mr. Fulton G. Kitson for the mass spectral identifications.

^{19}F NMR was performed on a Varian instrument by Mr. Thomas E. Beukelman. Interpretation was facilitated by our extensive reference library.

Ethylene Insertion. Pure **3** was heated at about 195 °C under 200–250 psi ethylene pressure for 8–12 h. For example, 535 g of $CH_3(CF_2)_5I$ was charged to the 400-mL shaker tube, which was then sealed, pressure tested, evacuated at −80 °C, and heated to 195 °C (vapor pressure 55 psi). Ethylene was admitted, and the pressure was maintained at 250 psi for 8.5 h. No further pressure drop occurred, showing that **4** was incapable of reacting with additional ethylene under these conditions. The bomb was cooled, vented, and discharged. Some material was lost in the feed lines, so the material balance was only 95%. Two such runs were combined and fractionated, yielding 37 g. (3.4%) of unreacted **3** and 995 g (84%) of product **4**. The 47 g of still residue was mostly **4**, but it also contained the telomers $CH_3(CF_2)_5(C_2H_4)_mI$, *m* = 2, 3, 4, identified by GC/MS.

With the other iodides **3**, 1–2% of starting material escaped conversion, and less than 1% of higher telomers were formed. Intermediate distillation cuts contained fragmentation products with fewer CF_2 groups than in **3**. Thus from **3**, *n* = 3, containing no detectable impurities, the following compounds were detected by GC/MS:

3, *n* = 1, 2
$CH_3(CF_2)_n(CH_2CH_2)_mI$
n = 1; *m* = 1
n = 2; *m* = 1, 5
n = 3; *m* = 1, 2, 4, 5, 8
n = 5; *m* = 1, 2, 3
n = 7; *m* = 1

In addition, **15**, $CH_3(CF_2)_3H$, $CH_2{=}CHCH_2CH_2CF_2CF_2CHFCH_2Cl$, 1,2,3,3-tetrafluorocyclobutene, and $C_{31}H_{63}I$ were detected. Total impurities were less than 2% of the product; such is the sensitivity of the GC/MS method.

Table III. Properties of $CH_3(CF_2)_nCH_2CH_2OH$, 6[a]

n	Bp, °C (Torr)	Mp, °C	Formula
5	87 (10)		$C_8H_8F_{10}O$
7	104 (10)		$C_{10}H_8F_{14}O$
9	130 (10)	53–54	$C_{12}H_8F_{18}O$
11	150 (10)	95–96	$C_{14}H_8F_{22}O$
13[b]		157–158	$C_{16}H_8F_{26}O$

[a] Satisfactory microanalyses for C and H, and in two cases F, were obtained for these compounds, except for $n = 13$. NMR spectra in CCl_3F were consistent with the structures. [b] The analysis agrees well with a dihydrate. Anal. Calcd: C, 25.7; H, 1.6. Found: C, 25.7; H, 1.5. The product also contains 0.5% I. This alcohol made satisfactory acrylate and methacrylate.

Table IV. Properties of $CH_3(CF_2)_nCH_2CH_2OCOC(R)=CH_2$, 7[a]

n	Method[b]	Bp, °C (Torr)	Formula
		A. Acrylates, R = H	
5	KS	109 (11)	$C_{11}H_{10}F_{10}O_2$
9	TE	90 (0.2)	$C_{15}H_{10}F_{18}O_2$
13	TE	128 (0.5)[c]	$C_{19}H_{10}F_{26}O_2$
		B. Methacrylates, R = CH_3	
3	KS	106 (21)	$C_{10}H_{12}F_6O_2$
5	KS	118 (10)	$C_{12}H_{12}F_{10}O_2$
7	KS	95 (0.8)	$C_{14}H_{12}F_{14}O_2$
9[d]	KS	105 (0.5)	
13[e]	TE	160 (1.0)[f]	$C_{20}H_{12}F_{26}O_2$

[a] Satisfactory NMR and IR spectra, and microanalyses for C and H (and in two cases F) were obtained, except as noted. [b] KS = potassium salt displacement; TE = transesterification. [c] Also mp 103–104 °C. [d] Not obtained pure. [e] The product is about 95% pure by GC. The principal impurities are $n = 11, 15$ methacrylates and $n = 11, 13$, and 15 iodides and alcohols. The carbon analysis is 1.3% low. [f] Also mp 103.0–103.5 °C.

Oleum Solvolysis of 4 to 6. Typically, the iodide **4**, $n = 7$ (100 g, 0.192 mol) was added dropwise to 300 g of 65% oleum maintained at 40–45 °C during 1.5 h. The mixture was maintained in that range for an additional 1.5 h. The viscous, deep bluish-green[18] mixture was transferred to an addition funnel with a 10-mm bore stopcock and added slowly to 700 mL of stirred water below 80 °C. Sodium bisulfite solution was added to the hydrolysis mixture to reduce the iodine. The mixture, now about 30% sulfuric acid, was refluxed (109 °C) for 2 h under a *wide-bore* condenser to prevent plugging by the solid alcohol hydrate which steam distills. A long glass rod was used for pushing that solid back into the flask. The lower layer was boiled briefly with fresh water. The crude alcohol, 64 g, was combined with 188 g of alcohol similarly obtained from 241 g of iodide, dried by refluxing with benzene under a water separator, and fractionated. The pure alcohol weighed 210 g, 78%. The forerun and tail cut, 40 g, were slightly less pure. The total yield was nearly quantitative.

With the iodide **4**, $n = 13$, the mixture became very viscous after about half the iodide had been added, but then it became gradually thinner. After the 3-h heating period, a little water was added *very cautiously* to thin the material so it could be poured. After the hydrolysis (as described), the alcohol was dried at 110 °C but not distilled. The yield was 99%.

(Meth)acrylates 7. A. By Transesterification. The alcohol **6**, $n = 9$ (44.1 g, 0.0866 mol), was mixed with 26.1 g (0.261 mol) of ethyl acrylate, 30.5 mL of benzene, a small drop of nitrobenzene, and 87 mg of 3,3′,5,5′-tetramethyldiphenoquinone, and refluxed under a fractionating column to remove water as its benzene azeotrope; 7.5 mL of benzene was removed. Then 0.2 mL of tetraisopropyl titanate was added with a syringe, and the mixture was slowly distilled to remove the benzene–ethanol azeotrope, bp 68 °C. When the head temperature could not be maintained below 75 °C, an additional 0.1 mL of titanate was added to ensure complete reaction. The benzene and excess ethyl acrylate were distilled out (24 mL), and the ester was distilled very rapidly under vacuum, yield 47.0 g (96.2%). It contained traces of benzene, ethyl acrylate, and unchanged alcohol which could be removed by topping through a short column.

Table V. Properties of $CH_3(CF_2)_nCH_2CH_2OSO_2Cl$, 8[a]

n	Bp, °C (0.5 Torr)	MS[b]	Formula
3[c]	72	Unusual	$C_6H_7F_6ClO_3S$
5	94	Unusual	$C_8H_7F_{10}ClO_3S$
7	110	Normal	$C_{10}H_7F_{14}ClO_3S$

[a] Satisfactory NMR spectra and microanalyses for C, H, and Cl were obtained for these compounds. [b] See Discussion section for comments on mass spectrometry. [c] Also sulfur. Anal. Calcd: 10.4. Found: 10.1.

The alcohol **6**, $n = 13$ (38.9 g, 0.05 mol), was dried azeotropically by refluxing with 25 g of methyl methacrylate, 35 mL of benzene, a small drop of nitrobenzene, and 100 mg of the quinone, treated with 0.2 mL of tetraisopropyl titanate, and the mixture was fractionated to remove methanol–benzene below 60 °C. Then 0.2 mL of water was added to destroy the titanate, and the product was stripped and distilled. The solid was redistilled through a short Vigreux column and the center cut was analyzed. The yield was about 50% because of thermal polymerization during the second distillation.

B. Displacement with Potassium Methacrylate. A mixture of iodide **4** with 2–3 mol of dry potassium (meth)acrylate in *dry* (molecular sieves) *tert*-butyl alcohol was refluxed for 14 h in the presence of a trace of tetramethyldiphenoquinone inhibitor. Some iodide escaped reaction. The mixture was drowned in water, and the aqueous layer was extracted with Freon 113. The combined organic layers were washed with water, dried, and distilled. Separation of unchanged iodide and by-product alcohol from the ester was difficult with $n = 3, 5, 7$, but impossible with $n = 9$. Therefore, transesterification procedure A is preferred.

Chlorosulfates 8. Chlorosulfonic acid (2.2 mol) was added dropwise to 1.0 mol of iodide at 40–45 °C during 1 h. The mixture was then maintained at 45–50 °C for 1 h. The escaping sulfur dioxide and hydrogen chloride were removed in a flowing water scrubber, and subliming iodine was retained by a wide-bore air condenser. The crude chlorosulfate was separated from suspended iodine by filtration on a dry, tared, sintered-glass funnel. The glassware was rinsed with Freon 113, which was then chilled to −30 °C and used to wash the iodine filter cake. Iodine is almost insoluble in this solvent at −30 °C. Iodine was recovered almost quantitatively. The solvent was evaporated and the chlorosulfate was distilled at reduced pressure; a small amount of the more volatile $CH_3(CF_2)_nCH_2CH_2Cl$ was collected separately. The high-boiling residue was mostly the alkylsulfuric acid **5**, as shown by infrared and by titration.

The chlorosulfates were identified by elemental analysis and NMR. The high-resolution mass spectra described in the text were obtained by Mr. R. D. Brown.

Olefins. The olefins **9**, $n = 5, 7$, were isolated from the methacrylate preparations with potassium methacrylate, simply by fractional distillation of the forerun. The olefin, $n = 11$, was prepared by refluxing a mixture of 216 g (0.3 mol) of iodide **4**, $n = 11$, with 22 g (0.37 mol) of 85% KOH in 150 mL of 95% ethanol for 19 h. The mixture was drowned in water, and the olefin was washed twice with hot water. The distilled product weighed 170 g (98.6%).

This olefin was oxidized to **10**, $n = 11$, by adding a solution of 105 g (0.67 mol) of potassium permanganate in 600 mL of water (90 °C) dropwise to 108.4 g (0.20 mol) of olefin at 70 °C during 1.5 h; the mixture was held at 70 °C for another 1 h. Slow addition of 70 g (0.67 mol) of solid sodium bisulfite was begun. When about half had been added, the temperature rose suddenly to 90 °C and the mixture sprayed out of the flask. Most of it was recovered and returned to the flask for completion of the bisulfite addition. Then 325 mL of concentrated hydrochloric acid was added cautiously, followed by enough additional bisulfite to destroy the remaining manganese dioxide. The mixture was then heated to 90 °C and cooled; the solid acid was collected and washed with 6 N hydrochloric acid. The solid was distilled rapidly at 30 mm to remove inorganic salts. When the solid distillate was remelted, an upper aqueous layer formed. Careful cooling froze the organic layer, and the water was decanted. The solid was then redistilled. The forerun was discarded, and the acid **10**, $n = 11$, was collected at 172 °C (28 mm), mp 92–93 °C, yield 53.5 g. At least some of the yield loss is attributable to the eruption.

Anal. Calcd for $C_{13}H_4F_{22}O_2$: C, 25.6; H, 0.7. Found: C, 25.9, H, 1.0.

Table VI. Properties of $CH_3(CF_2)_nCH{=}CH_2$, 9[a]

n	Bp, °C (Torr)	Mp, °C
3[b]		
5	130 (760)	
7	110 (147)[c]	
11[d]	126 (27)	36–37
13	143 (20)	75–76
15[e]	142–157 (10)	91–92
17+[f]		

[a] The first compound was identified by GC/MS only; the second and third by NMR only. The fourth and fifth compounds gave satisfactory C and H microanalyses, as well as consistent NMR spectra. [b] Detected as a by-product from the reaction of **4**, $n = 3$, with potassium methacrylate. [c] Also bp 90 °C (51 mm). [d] Prolonged refluxing of **4**, $n = 11$, with excess pyridine caused only partial dehydroiodination. [e] The product was a mixture of roughly equal amounts of $n = 13$ and 15. [f] A mixture of olefins, $n = 11$–25, was prepared from the mixed **4** prepared with ethylene insertion into the still residues from **3**. The presence of these olefins was detected by the GC analysis, but they were not otherwise characterized.

Preparation of 1,1,2,2-Tetrafluoro-1,4-diiodobutane (12).[9] A 400-mL shaker tube (Hastelloy C) was charged with 509 g (2.0 mol) of iodine, evacuated, and mounted in its heater on the shaker. A little TFE was admitted, and the bomb was heated to 125 °C. Then TFE was fed as rapidly as possible consistent with maintaining the temperature below 160 °C. When the theoretical amount of TFE had been absorbed, the pressure rose rapidly to 150 psi. The bomb was cooled to 100 °C and held for 1 h under 150 psi TFE pressure. Then at −80 °C, 100 g (4 mol) of ethylene was condensed into it. It was reheated to 150 °C, pressure about 5000 psi, and held for 6–8 h at 150 °C and a further 6–8 h at 165 °C. The product, a mixture of solid and liquid, was cooled to 0 °C and filtered; the solid was washed with a little cold chloroform. The solids from four such runs melted variously at 112–115 °C. The combined chloroform washes were evaporated and chilled to remove more solid. The combined liquids (four runs) were distilled to remove **11** and the more volatile by-products, then pure **12**, and finally the 2:1 adduct. 1,1,2,2-Tetrafluorocyclobutane was a major by-product, and the following trace compounds were also identified by GC/MS: HCF_2CF_2I, $CH_2{=}CHI$, $CH_3CH_2CF_2CF_2CH{=}CH_2$, CH_3CH_2I, $HCF_2CF_2CH_2CH_2I$, $I(CF_2)_4I$, and ICH_2CH_2I. The yield of pure **12** was 1792 g (59%), bp 85 °C (23 mm), and 306 g (9%) of 2:1 adduct was formed. The yield might be improved by feeding ethylene gradually from a compressor at pressures lower than the 5000 psi used here; we had no compressor. The optimum temperature was not determined.

Borohydride Reduction of 12. A solution of 3.8 g (0.1 mol) of sodium borohydride in 100 mL of methanol containing 0.1 g of sodium hydroxide was added to a solution of 38.2 g (0.1 mol) of **12** in 100 mL of methanol at 0 °C during 1 h under nitrogen. The next day the mixture was drowned in water. The lower layer was washed with dilute sodium bisulfite solution and water, then dried ($CaCl_2$). The crude **13** contained about 20% of unchanged **12**, but otherwise only trace impurities. The yield was about 66%. The product was distilled, bp 78.5 °C (202 mm) or 56 °C (51 mm). The center cut was identified by NMR and mass spectrum as $ICH_2CH_2CF_2CF_2H$, **13**. The method is potentially valuable for reducing other fluoroalkyl iodides R_FI to R_FH.

Dehydroiodination. The diiodide **12** (76.4 g, 0.2 mol) was added during 12 min to a solution of 25 g (0.25 mol) of dry triethylamine in 50 mL of dry *tert*-butyl alcohol. The mixture was then heated slowly. Between 40 and 70 °C, it turned black. It was refluxed (82 °C) for 45 min, and a sample was drowned in dilute hydrochloric acid; half of the **12** had not reacted. An additional 25 g of triethylamine was added and the mixture was refluxed for 30 min. The mixture was drowned in dilute acid, and the lower layer was washed and dried (45 g), then distilled. The olefin cut weighed 23.4 g, accompanied by 11.5 g of starting **12** and 5.5 g of tarry residue. The olefin cut was fractionated to yield a host of volatile impurities in the forerun, and pure **14**, bp 90–91 °C (760 mm), yield 25%. It was identified by NMR and mass spectrum.

An attempt to eliminate hydrogen iodide from **12** with potassium hydroxide in isopropyl alcohol caused extensive destruction, with formation of $CH_2{=}CHCF_2CF_2H$, $CH_2{=}CHCF_2COOK$, and other products. The yield of olefin was miserable. Perhaps a strong base in an aprotic solvent (Me_2SO, dioxane) would effect a satisfactory elimination without attack on the other iodine atom.

Diimide reduction of **14** was accomplished by adding 0.2 mol of 95% hydrazine to a mixture of 20 g (0.079 mol) of **14**, 100 mL of methanol, and 0.2 g (2 mmol) of cuprous chloride. The temperature rose to 35 °C. The mixture was cooled strongly while 28.3 g (0.25 mol) of 30% hydrogen peroxide was added dropwise in 37 min at 30–40 °C. The yellow solution was stirred for 2 h at ambient temperature; a small lower layer was noted. The mixture was diluted with 500 mL of ice water containing 2 mL of concentrated hydrochloric acid, the mixture was extracted with three portions of *o*-dichlorobenzene, and the extract was stripped at 100 mm into a −80 °C trap until the solvent began to boil. The trap contents were then distilled. The center cut (2.1 g), bp 40–45 °C (150 Torr), was 81% $CH_3CH_2CF_2CF_2I$ (**15**), 8% **14**, and the balance other materials (NMR). The outer cuts totaled 1.9 g. The yield of **15** was 10% in this single attempt.

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Registry No.—**2**, 420-47-3; **3** (n = 3), 61951-28-8; **3** (n = 5), 61915-74-0; **3** (n = 7), 61915-75-1; **3** (n = 9), 61915-76-2; **3** (n = 11), 61915-77-3; **3** (n = 13), 61915-78-4; **3** (n = 15), 61915-79-5; **4** (n = 3), 61915-80-8; **4** (n = 5), 61915-81-9; **4** (n = 7), 61915-82-0; **4** (n = 9), 61915-83-1; **4** (n = 11), 61915-84-2; **4** (n = 13), 61915-85-3; **4** (n = 15), 61915-86-4; **6** (n = 5), 61915-87-5; **6** (n = 7), 61915-88-6; **6** (n = 9), 61915-89-7; **6** (n = 11), 61915-90-0; **6** (n = 13), 61915-91-1; **7** (R = H; n = 5), 61915-92-2; **7** (R = H; n = 9), 57678-90-7; **7** (R = H; n = 13), 61915-93-3; **7** (R = Me; n = 3), 61915-94-4; **7** (R = Me; n = 5), 61915-95-5; **7** (R = Me; n = 7), 61915-60-4; **7** (R = Me; n = 9), 61915-61-5; **7** (R = Me; n = 13), 61915-62-6; **8** (n = 3), 61915-63-7; **8** (n = 5), 61915-64-8; **8** (n = 7), 61915-65-9; **9** (n = 5), 61915-66-0; **9** (n = 7), 61916-67-1; **9** (n = 11), 61915-68-2; **9** (n = 13), 61915-69-3; **9** (n = 15), 61915-70-6; **10** (n = 11), 61915-71-7; **12**, 755-95-3; **13**, 61915-72-8; **14**, 33831-83-3; **15**, 61915-73-9; vinylidene fluoride, 75-38-7; TFE, 116-14-3; ethylene, 74-85-1; ethyl acrylate, 140-88-5; methyl methacrylate, 80-62-6; potassium methacrylate, 6900-35-2.

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(13) For references, see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 257.
(14) I am indebted to Mr. J. L. Robinson for this experiment.
(15) The liquid in this tube is a mixture of TFE and telogen **2**. By holding it at −20 °C with the vent open, the TFE evaporated with little loss of **2**. The amount of unreacted TFE was determined by the difference in volume between the two liquid measurements.
(16) I am indebted to Mr. Samuel Hearn and his staff in our High Pressure Laboratory for performing the experiments in shaker tubes.
(17) The percentage figures are based on the total weight of telomers $n = 5$ and higher.
(18) The bluish color suggests the presence of I_2^+, discovered by R. J. Gillespie and J. B. Senior, *Inorg. Chem.*, **3**, 440 (1964), and E. E. Aynsley, N. N. Greenwood, and D. H. W. Wharmby, *J. Chem. Soc.*, 5369 (1963).