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Free-Radical Telomerization of Tetrafluoroethylene in Supercritical Carbon Dioxide

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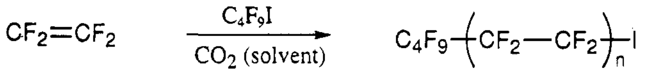
Perfluoroalkyl iodides are commercially important intermediates in the manufacture of many fluorinated compounds. They are useful in the synthesis of fluorinated olefins and fluorinated alcohols and for the manufacture of fluorinated acrylate and methacrylate monomers which find many applications as surfactants and in low surface energy coatings. There are many examples of perfluoroalkyl iodide syntheses employing tetrafluoroethylene (TFE) telomerizations with low molecular weight perfluoroalkyl iodide telogens. Researchers have detailed telomerizations initiated by thermal energy,[1] γ-rays,[2] laser light,[3] and UV light[4] and even processes catalyzed by transition-metal salts.[5] Telogens commonly employed in these reports include iodotrifluoromethane, iodopentafluoroethane, 2-iodoperfluoropropane, and perfluorobutyl iodide in addition to IF_5/I_2 ("IF")[6] as well as others.

Tetrafluoroethylene is a difficult material to handle both on an industrial scale and in the laboratory.[7] TFE forms explosive mixtures with air, can disproportionate violently in the absence of air to form elemental carbon and carbon tetrafluoride, and must be kept scrupulously free of oxygen to prevent the formation of shock-sensitive polymeric peroxides. Through efforts to facilitate safer handling of TFE, researchers at DuPont have recently discovered that TFE may possibly be handled more safely as a mixture with carbon dioxide.[8] The results of this work suggest that, in the presence of sufficient CO_2, TFE does not form explosive mixtures with air and that TFE and CO_2 form a "pseudoazeotrope". As a result, removal of a gaseous TFE/CO_2 mixture from a high-pressure cylinder containing compressed gas and liquid components would not result in a dramatic enrichment of TFE concentration (a potentially unsafe condition) in the cylinder or in downstream piping. Although this potentially important discovery might allow for safer shipping and handling of TFE, it would be ideal if the monomer could be used directly without removal of CO_2.

Our work[9] and the work of others[10] has shown that carbon dioxide is an excellent medium in which to perform free-radical reactions. In addition, our recent report of the telomerization of vinylidine fluoride in supercritical carbon dioxide[11] further demonstrates the utility of this medium for free-radical-based syntheses. We therefore present the telomerization of TFE employing perfluorobutyl iodide as telogen in supercritical carbon dioxide as a means of synthesizing perfluoroalkyl iodides. A general scheme for the telomerization of TFE in CO_2 is depicted in Scheme 1.

Tetrafluoroethylene telomerizations initiated by azobis(isobutyronitrile) (AIBN) were conducted at 20 w/v % monomer in a 25-mL high-pressure view cell fitted with a full-bore rupture disk (see Figure 1). The reactor was housed in a ¼-in. steel enclosure to protect personnel and equipment in the event of an explosion. Reaction progress and phase behavior were visually monitored over the course of the reaction using a fiber-optic borescope and television monitor. The ratio of monomer to telogen was controlled by varying the amount of perfluorobutyl iodide charged to the cell. In a typical reaction, the reactor was evacuated and then purged with argon. AIBN (Kodak; recrystalized twice from methanol before use) was placed in an addition chamber (Figure 1), and the chamber was purged with argon and sealed. Perfluorobutyl iodide (PCR; distilled from triethylaluminum) was added to the reactor via syringe under a positive argon pressure. The cell was then cooled to well below 0 °C in a dry ice/acetone bath, and the desired amount of monomer was condensed in as a mixture with carbon dioxide (TFE/CO_2 mixture supplied by DuPont). The safety enclosure was then closed and secured. The temperature was raised to 68 °C and allowed to equilibrate before CO_2 (research grade; Air Products; transferred using an Isco Model No. 260D automatic syringe pump) and initiator were added simultaneously through the initiator addition chamber to the desired reaction pressure of 345 bar. After 4 h the cell was cooled in an ice bath, the CO_2 vented, and the product isolated. For thermally initiated reactions, the cell was charged with telogen, monomer, and CO_2 (similar to the AIBN-initiated reactions) and then the cell was heated to 180 °C for 3 h, cooled, and vented to the atmosphere. Five grams each of CO_2 and TFE were employed, and again the monomer to telogen ratio was controlled by varying the amount of perfluorobutyl iodide employed. Number-average molecular weights and molecular weight distributions for all reactions were determined by gas chromatography−mass spectrometry analyses (HP5890 Series II oven with 25-m HP-1 column; HP5971A mass selective detector) on samples dissolved in 1,1,2-trichloro-2,2,1-trifluoroethane. Product yields were determined gravimetrically.

Scheme 1



Reactions Initiated with AIBN. For reactions initiated with AIBN, the introduction of CO_2 and initiator to the heated reaction vessel (already containing monomer and telogen) resulted in a homogeneous solution occupying the entire reactor volume. As the reaction proceeded at the reaction temperature of 68 °C and pressure of 345 bar (5000 psig), the solution became cloudy and soon a precipitate was observed. After venting, products were isolated as slightly yellow liquids or waxy yellow solids depending on the monomer to telogen ratio employed. Product distributions exhibited number-average molecular weights of 620−960 and molecular weight distributions (DP_w/DP_n)[12] of 1.4−1.6. In most cases, reaction products precipitated because the higher molecular weight fractions exhibit low solubility in CO_2 (at the relatively low temperature of 68 °C) owing to their ability to crystallize. At low monomer to telogen ratios (e.g., 0.91), the solution remained homogeneous throughout the course of the reaction due to the low molecular weight of the products formed. A plot of number-average degree of telomerization versus telogen concentration over monomer concentration (shown in Figure 2) for AIBN-initiated reactions is linear, the slope of which yields an average chain transfer constant of 0.23 ± 0.01 which is comparable wih previously reported values.[13] Because the monomer

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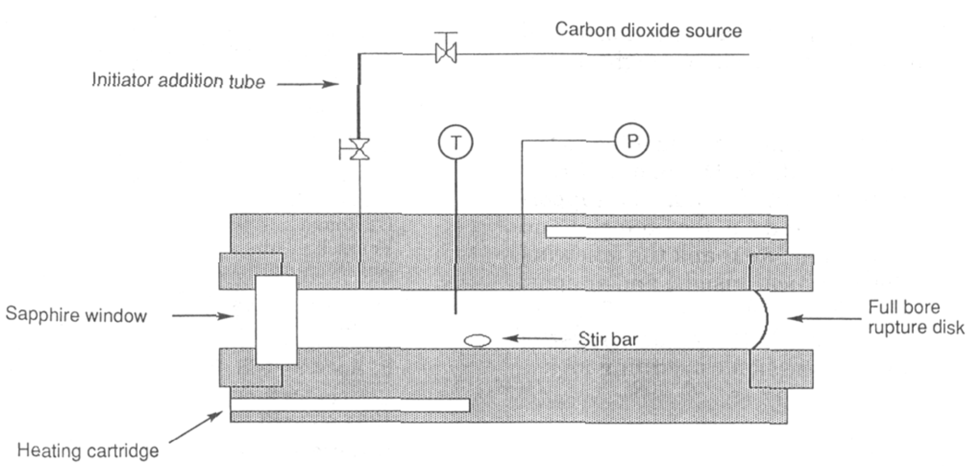

Figure 1.

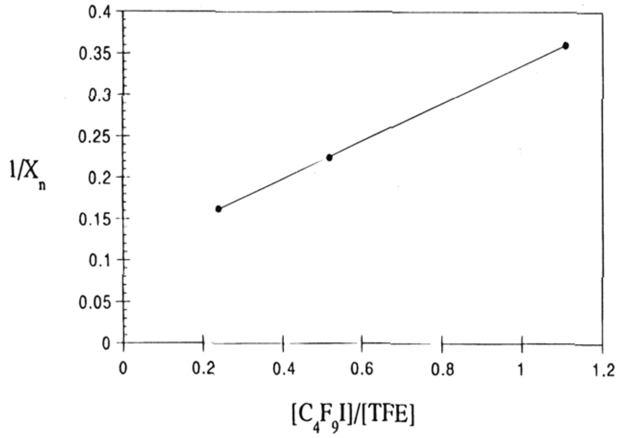

Figure 2.

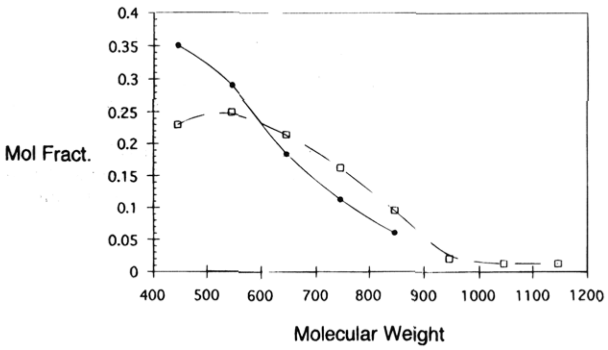

Figure 3.

Table 1

[monomer]/[telogen]	yield (%)	M_n	MWD (DP_w/DP_n)
1.6	88	570	1.35
1.5	87	590	1.38
1.8	86	630	1.38
2.2	78	650	1.44

to telogen ratio is a function of conversion for all but "azeotropic" systems ($C_{tr} = 1$), further analyses involving reactions allowed to proceed only to low conversion (e.g., <5%) would allow calculation of explicit chain-transfer constants. For systems where chain-transfer constants are relatively near 1 (such as those presented here), a reasonable estimate of chain-transfer constants may be obtained even at higher conversions. Further investigation of chain-transfer constants may be the subject of a future publication.

Gravimetrically determined product yields for telomerizations initiated with AIBN were inconsistent and irreproducible. A possible explanation might be chain transfer to initiator (primarily from the perfluorobutyl radical) which could yield predominantly gaseous products (e.g., C_4F_9H) that would be lost upon venting. There are several reports[14] in the literature on the high rate of hydrogen abstraction by fluorinated radicals; indeed hydrocarbons such as hexanes or acetic acid can be used as chain-transfer agents in telomerizations of tetrafluoroethylene and other fluoromonomers.[15]

Thermally Initiated Telomerizations. When TFE/CO_2 was condensed into the reaction vessel at low temperature, the result was a lower telogen-rich liquid phase and an upper gaseous phase rich in CO_2 and monomer. Upon warming to much above room temperature a homogeneous solution occupied the entire reactor volume. The reaction mixture remained homogeneous during the entire course of the reaction at 180 °C until cooling, at which time the telomer product gradually precipitated with decreasing temperature. Reaction pressures at 180 °C were a function of telogen concentration (higher telogen concentrations gave lower pressures) and ranged from 165 to 220 bar. Conversions obtained for these reactions were all greater than 75% (based on gravimetric analysis), and products ranged from clear liquids to waxy white solids depending on molecular weight. Yields decreased with increasing monomer to telogen ratio—consistent with behavior expected for a system in which the telogen also serves as the initiator. Two of the product distributions with number-average molecular weights of 570 and 630 (MWD = 1.35 and 1.38, respectively) are depicted in Figure 3.

Table 1 lists the monomer to telogen ratios, yields, product number-average molecular weights, and molecular weight distributions for four representative reactions. A plot of $1/X_n$ vs [telogen]/[monomer] is linear, the slope of which yields an average chain-transfer constant of 0.5 ± 0.2, which is also consistent with previously reported values.[11]

In conclusion, carbon dioxide is an exceptional medium in which to perform free-radical telomerizations of tetrafluoroethylene using perfluoroalkyl iodide telogens without chain transfer to solvent which plagues most all other solvent choices. It is likely that, because of the propensity of highly fluorinated radicals to chain transfer to hydrocarbons, AIBN may not be a suitable free-radical initiator for this reaction but that processes utilizing other modes of initiation are viable. Thermally initiated telomerization of tetrafluoroethylene in supercritical carbon dioxide is a useful method for the preparation of perfluoroalkyl iodides with controlled molecular weights and narrow molecular weight distributions.

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