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Communications to the Editor

Homogeneous Free-Radical Polymerizations in Carbon Dioxide. 3. Telomerization of 1,1-Difluoroethylene in Supercritical Carbon Dioxide

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Herein we describe the homogeneous synthesis of fluorinated telomers in supercritical carbon dioxide. Recent discoveries from our laboratories have shown the viability of using supercritical CO_2 as a solvent medium for the homogeneous solution polymerization of various fluorinated acrylic[1] and fluorinated styrenic[2] monomers, a procedure prior to this discovery achievable in relatively few solvents such as chlorofluorocarbons (CFC) and α,α,α-trifluorotoluene. In addition, several copolymers (with nonfluorinated comonomers) were synthesized homogeneously in supercritical CO_2 as well.[1] These highly fluorinated copolymers were also soluble in traditional organic solvents such as tetrahydrofuran. The decomposition reactions of diacyl peroxides,[3] (phenylazo)-triphenylmethane,[4] and azobis(isobutyronitrile)[5] in supercritical CO_2 demonstrated the effectiveness of carbon dioxide as an inert solvent medium for free-radical chemistry. In addition to being an environmentally responsible solvent choice, we have shown that supercritical CO_2 offers several advantages as a solvent for homogeneous polymerizations: low solution viscosity (no Tromsdorff effect), an effectively inert solvent medium (no detectable chain transfer to solvent), and solvent strength tunability (dielectric constant range of 1.05–1.5 at 60 °C from 100 to 500 bar).[5] In addition to being a good solvent choice for homogeneous polymerizations of certain fluorinated monomers, we have also described paradigms for replacing water and organic-dispersing media with CO_2 for heterogeneous emulsion and suspension polymerizations.[6,7] Previously Hagiwara,[8] Hartmann,[9] and Huvard[10] have described dispersion or precipitation polymerizations in CO_2. For supercritical alkanes, Beckman and coworkers[11,12] have described microemulsion processes in solvents such as ethane and propane.

One major economic advantage to using SCF solvents for polymerizations is the elimination of elaborate solvent purification processes, thereby providing an environmentally responsible alternative process that could offer substantive energy savings when considering the relative ease with which solvent can be separated from the product.[13] The solvent density, a property readily adjustable with a SCF solvent, can be manipulated with relatively slight changes in pressure, thereby facilitating efficient solvent separation schemes.[13] Integration of reaction and separation processes is possible as well owing to the variability of solvent strength (a density-dependent property). Should products of a reaction (e.g., polymers of a particular molar mass) be insoluble in the SCF solvent at reaction conditions, product removal and control of the reaction kinetics can be simplified by consolidation of the reactor and separation equipment into a single vessel.

The telomerization of fluorinated olefins began with the work of Haszeldine,[14] who showed that tetrafluoroethylene (TFE) could be treated with trifluoroiodomethane to yield relatively low molecular weight, functionalized oligomers (i.e., telomers). Both Haszeldine and Ashton et al.[15] carried out telomerizations in bulk or in the gas phase and initiated their reactions using UV light. Other TFE telomerizations were initiated using laser light,[16,17] γ-rays,[18] or were initiated thermally ($T > 200$ °C).[19,20] Various telogens were used including trifluoroiodomethane, dibromodifluoromethane, 1,1-difluoroethyl iodide, and molecular iodine. Reactions were typically carried out in sealed autoclaves with either an initial monomer charge or with stepwise addition. 1,1-Difluoroethylene (vinylidene fluoride, VF_2) has also been shown to telomerize in the presence of chain-transfer agents. Hauptschein et al.[21] used a series of fluorinated iodoalkanes and bromoalkanes as telogens and achieved degrees of polymerization from 1 to 8. Again monomer and telogen were mixed in a sealed autoclave and heated to 180 °C or higher. Tarrant and Lilyquist[22] synthesized several telomeric products of VF_2 using 1,2-dibromo-2-chloro- and 1,2-dichloro-2-iodo-1,1,2-trifluoroethane. Products obtained were of a relatively low degree of polymerization but were produced in high yield. As with Hauptschein et al.,[21] no initiating catalysts were added; reactions were performed in bulk in sealed autoclaves at relatively high temperatures. Modena et al.[23] telomerized VF_2 with 1,2-dibromotetrafluoroethane using various peroxide initiators. The presence of radical initiators enabled the reactions to proceed under relatively mild conditions.

According to the literature, telomerizations are commonly performed in the bulk without the use of a solvent. The origins of this practice are unclear and may be related to the poor solubility of fluorocarbons in solvents other than chlorofluorocarbons (CFCs such as 1,1,2-trichloro-1,2,2-trifluoroethane would lead to chain transfer to solvent, especially at elevated temperatures). Also, as the telomerizations were conducted in sealed autoclaves, no observations regarding phase behavior have been reported; hence, no influence of solution density on polymerization variables have been explored. Herein, we describe the use of supercritical CO_2 as a solvent for the telomerization of VF_2 under well-controlled homogeneous conditions. VF_2 is a safe, readily available fluorinated monomer that also exhibits interesting regiochemistry upon telomerization.

The telogen, perfluorobutyl iodide (PCR) was distilled over triethylaluminum under an argon atmosphere and was subsequently stored under an argon atmosphere in the dark. Azobis(isobutyronitrile) (AIBN; Kodak) was recrystallized twice from ethanol prior to use. Tetrahydrofuran (THF; EM Science, >99.5%) and toluene (EM Science, reagent grade) were used as received. 1,1-Difluoroethylene (Aldrich) was transferred from a lecture bottle to a stainless steel syringe pump (High Pressure Equipment Inc. Model 37-6-30) and charged to the reactor

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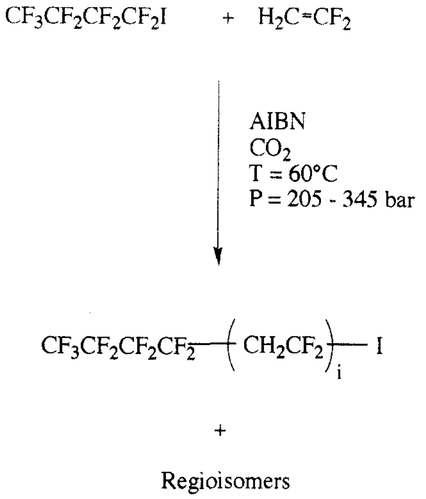
Scheme 1. Telomerization of Vinylidene Fluoride in Supercritical CO_2



without further treatment. Carbon dioxide (research grade; Air Products) was transfered to an Isco Model No. 260D automatic syringe pump and was used as received.

AIBN (50 mg) was added to a 10-mL stainless steel reactor equipped with sapphire windows.[24] The cell was purged with argon and weighed on a Mettler PM4000 balance. A measured volume of the telogen was transferred via a cannula to the high-pressure cell. The cell was weighed again to ensure the proper amount of telogen was added. VF_2 was added using the high-pressure syringe pump, and the cell was weighed to verify the amount of monomer addition. The reactor was pressurized to approximately 60 bar with carbon dioxide, and the cell was heated to 60 °C. A metered amount of carbon dioxide was then added via the syringe pump to achieve the final desired system pressure. Stirring was maintained using a magnetic stir bar, and solution homogeneity (i.e., no second phase) was visually verified over the course of the reaction. After 24 h the cell was immersed in an ice water bath. The contents of the cell were slowly vented through 20 mL of THF contained in a round-bottomed flask that was immersed in a dry ice/isopropyl alcohol bath. Toluene (1.0 mL) was added to the THF solution as an internal standard for chromatographic assay. After venting was complete, the cell was brought to room temperature, weighed, rinsed twice with the THF solution, and weighed again to determine the percent conversion. The extract solution was then analyzed using capillary GC (HP5890 Series II oven with a 25-m HP-1 column). Peak assignments were made with the aid of a mass selective detector (HP 5971A).

The telomerization of VF_2 with perfluorobutyl iodide is illustrated in Scheme 1. AIBN was added to initiate this reaction under these relatively mild thermal conditions ($T = 60$ °C). In addition to the normal 2,1-addition (heat-to-tail) products, it was also possible to see defect 1,2-addition (head-to-head) products. A chromatogram of the THF extract solution with peak assignments is shown in Figure 1. Peak assignments for the normal addition (i.e., 2,1-addition) telomers were relatively easy to identify for low degrees of polymerization (DP = 1–3) as signals from the intact molecular ion corresponding to the molecular weight of the products appeared (i.e., 410 g/mol for DP = 1; 474 g/mol for DP = 2, etc.) as well as ion fragmentation products expected for the regioisomers in question (i.e., $-CH_2I$ fragments were not observed). Telomers end-capped with $-CH_2I$ groups (labeled 2′,3′, etc., in Figure 1) eluted after their normal addition regioisomers and were characterized by fragmentation peak analysis which showed $-CH_2I$ and $-CF_2CH_2I$ fragments. Several other relatively minor products eluted from the extract solution and were tentatively identified as other telomeric regioisomers. Experiments involving the chromatographic separation of the products followed by ^{13}C and/or ^{19}F NMR analysis to provide more definitive identification are currently underway. None of the fragmentation patterns observed provided any evidence of CO_2 incorporation into the telomers. In addition ^{13}C NMR analysis of the product mixture did not reveal the presence of a carbonyl carbon, which further demonstrates the effectively inert nature of CO_2 in free-radical chemistry.

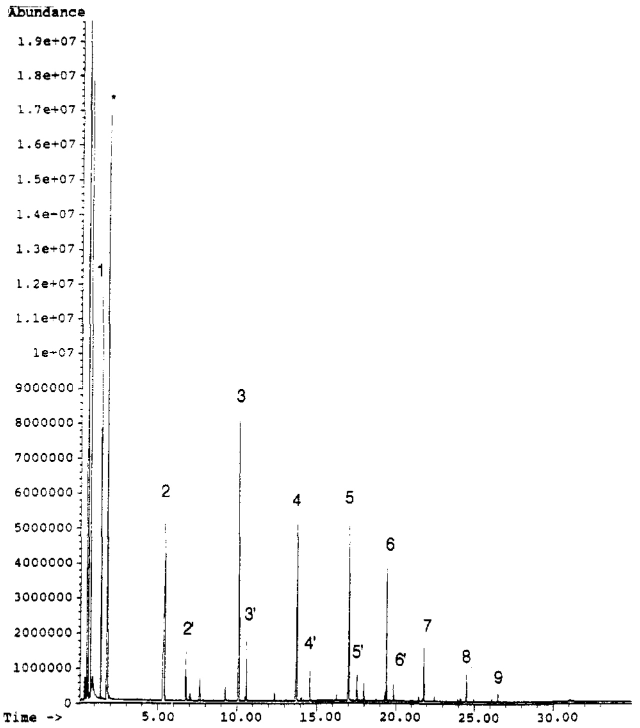


Figure 1. Gas chromatogram of a THF extract solution. The numbers correspond to the degree of polymerization. The primes denote CH_2I end-capped telomers. The asterisk indicates toluene.

Table 1. Summary of Reaction Conditions and Results for the Telomerization of VF_2 in Supercritical CO_2 at $T = 60$ °C in a 10-mL Stainless Steel View Cell for 24 h[a]

fluid density (g/cm^3)	initial pressure (bar)	mass of VF_2 (g)	mass of C_4F_9I (g)	M_w	M_w/M_n	convn (%)
1.24	340	3.8	1.6	608	1.051	35
1.20	280	4.0	2.2	588	1.048	32

[a] Densities were calculated from the reagent masses added to the cell and volume measurements from the Isco syringe pump used for CO_2 addition.

Experimental conditions are summarized in Table 1, and detailed molar mass distributions calculated by integrated chromatographic peak areas (using FID detection) are shown in Figure 2. The weight percentages were calculated assuming equal detector response factors for each telomer on a unit mass basis. The distribution of telomers is maximum at relatively low degrees of polymerization (DP = 2 or 3) and extends to products with degrees of polymerization up to DP = 9 for both experiments. The regioselectivity exhibited is primarily directed toward normal head-to-tail (2,1-addition) as opposed to the defect head-to-head (1,2-) addition products. For degree of polymerization, DP = 1, no head-to-head telomers were detected by chromatographic assay. However, for the higher molecular weight telomers the

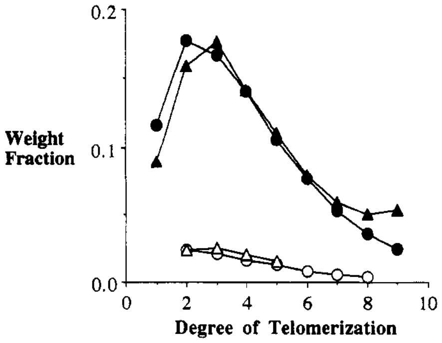


Figure 2. Weight fraction of telomeric products of VF_2 in supercritical CO_2: (●) 285 bar, normal addition; (▲) 340 bar, normal addition; (○) 285 bar, defect addition; (△) 340 bar, defect addition.

selectivity toward normal addition was relatively constant at 20:1. The molar mass and the molar mass distribution of products appear to be sensitive to solvent density. As shown in Figure 2, telomers of higher molar mass are achieved at higher pressures, probably as a result of the negative activation volume generally associated with propagation. Future work is focused on the influence of solvent density on the molar mass and molar mass distribution of the telomers. Manipulation of solvent density could potentially afford a means to remove telomers of a certain kinetic chain length from further reaction and to establish a viable reaction/separation pathway.

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