Organic LETTERS

Letter

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Synthesis of Fluorinated Telechelic Diols Based on 3,3,3-Trifluoropropene as Precursors of Well-Defined Fluoropolymers

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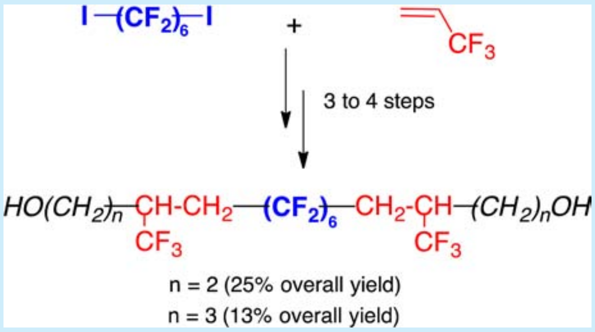
Supporting Information

ABSTRACT: Original fluorinated α,ω-diols containing 3,3,3-trifluoropropene (TFP) units were synthesized. The first step dealt with the radical telomerization of TFP with 1,6-diiodoperfluorohexane. Isolated $I(TFP)R_F(TFP)I$ diadduct was subsequently reacted with ethylene, and then a two-step hydrolysis gave rise to α,ω-diols in 25% overall yield. The other strategies dealing with the radical addition of $I(TFP)R_F(TFP)I$ onto allyl alcohol or allyl acetate led to α,ω-diols in 13% overall yield. These diols display satisfactory thermal stabilities and low T_g (ca. −60 °C).



Fluorinated polymers are niche macromolecules endowed with high thermal stability, chemical inertness (to acids, bases, and solvents), low dielectric constants, low water absorptivity, good resistance to oxidation and aging, low flammability, and very interesting surface properties.[1] Hence, despite their high price, fluoropolymers are involved in many applications such as aerospace and aeronautical engineering, protective and antiadherent coatings, Li ion batteries (binders, separators, and polymer electrolytes), optical fibers, paints, surfactants, fire fighting foams, high-performance elastomers, fuel-cell membranes, electrical isolators, and O-rings.

Well-architectured polymers are synthesized from controlled radical polymerization,[2] polycondensation, or polyaddition. These last two processes require α,ω-difunctional precursors, also called telechelics (i.e., the functional groups are located at both extremities of the chains), to obtain high molecular weight materials with satisfactory properties.[3] The synthesis of fluorinated telechelics is well-described in the literature[4] (e.g.,., they can be prepared from α,ω-diiodides[5]). Fluorinated telechelics bearing the fluorinated group in a lateral position from the polymeric backbone are exploited for their enhanced surface properties. By contrast, those possessing a fluorinated chain within the backbone exhibit much better resistance toward aggressive media, UV radiation, and aging.

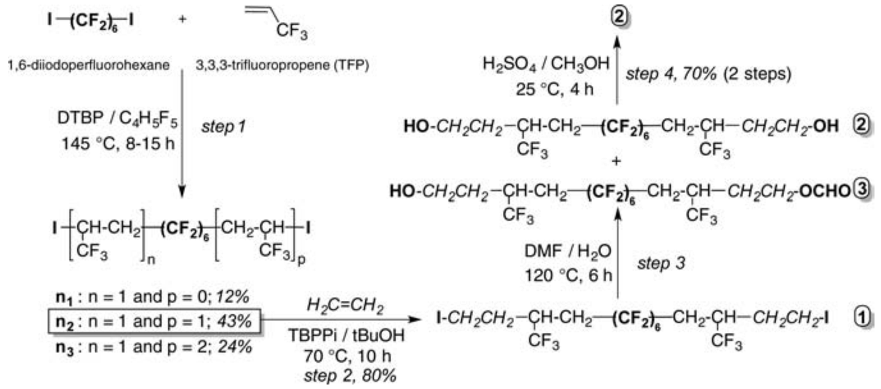
To date, only four kinds of fluorinated telomers are marketed: (i) Krytox by the DuPont de Nemours Company,[6] (ii) Fomblin oligomers ranging from 1000 to 4000 g/mol by the Ausimont Company, now Solvay-Specialty Polymers,[7] (iii) Demnum oligomers commercialized by the Daikin Company,[8] and (iv) Aflunox supplied by Nippon Mektron, now Unimatec.[9]

Among fluorinated telechelics, α,ω-diols appear as useful preprecursors for the synthesis of fluorinated polyurethanes,[10] polyesters,[11] triazines (via telechelic cyanates[12]), and cured networks (via telechelic (meth)acrylates[13]). In addition, they are also used as macroinitiators for the ring-opening polymerization of lactides to prepare polylactide-*b*-R_F-*b*-polylactide triblock copolymers.[14]

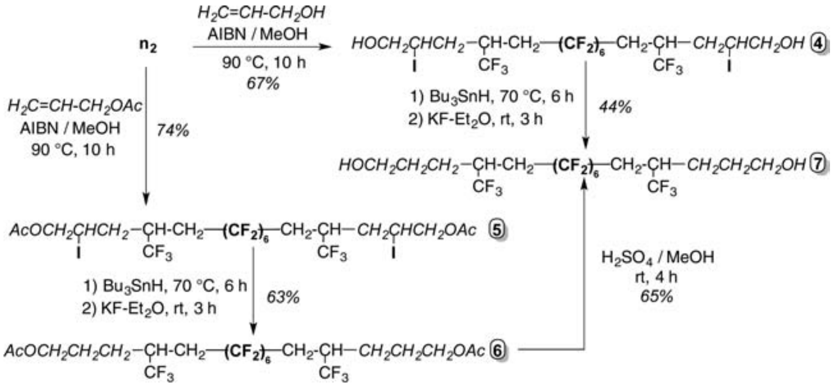
The synthesis of fluorinated α,ω-diols by direct fluorination of their hydrogenated counterparts has been successfully achieved in pilot plants.[15] Fluorinated α,ω-diols containing vinylidene fluoride and hexafluoropropene base units have been synthesized by Chan et al. (e.g.,., $HOCH_2CF_2(CH_2CF_2)_p[CF(CF_3)CF_2]_qCF_2CH_2OH$).[16] Li and Chen have also succeeded in preparing low fluorine content α,ω-diols of type $[HOCH_2CH(I)CH_2]_2CF_2$ from the addition of diiododifluoromethane to allyl alcohol.[17] Nevertheless, fluoro diols are scarce, and few are commercially available. Within the framework of our research toward the synthesis of well-defined fluorinated telechelics,[18] we wish to report herein three strategies to prepare fluorinated α,ω-diols based on 3,3,3-trifluoropropene (TFP). In contrast to tetrafluoroethylene (TFE), vinylidene fluoride (VDF), chlorotrifluoroethylene (CTFE), and trifluoroethylene (TrFE), which are the most well-known fluoroalkenes, 3,3,3-trifluoropropene has not been used in many radical reactions or telomerization.[2] 3,3,3-Trifluoropropene is the precursor of a commercially available fluorinated silicone marketed by the Dow Corning Co. under the trade name

Received: May 21, 2014
Published: June 24, 2014

Scheme 1. Synthesis of Fluorinated Telechelic Diol through Ethylenation of α,ω-Bis(TFP) Telomer



Scheme 2. Synthesis of Fluorinated Telechelic Diols from the Reaction of α,ω-Bis(TFP) Telomer with Allyl Acetate or Allyl Alcohol



Silastic. Thanks to this fluoroalkene precursor, Silastic can preserve interesting properties at low temperature.

The first common step (Scheme 1, step 1) dealt with the radical telomerization of TFP with 1,6-diiodoperfluorohexane. Di-*tert*-butyl peroxide (DTBP) was chosen as the radical initiator. The reactions were carried out in 160 or 300 cm^3 Hastelloy autoclaves at 145 °C, transferring gaseous TFP monomer into an IR_FI/peroxide/1,1,1,3,3-pentafluorobutane solution. The total product mixture was analyzed by GC before being distilled to obtain the different telomers (Figures S1−S3, Supporting Information, SI), which were characterized by NMR spectroscopy. From an extrapolation of our previous work,[18] the most suitable reaction conditions were chosen as follows: $[DTBP]_0/[TFP]_0$= 6 mol %, $R_0 = 0.35$, with reaction time <15 h. In the presence of 2.5 equiv of TFP to $I-C_6F_{12}-I$ and given that the BDE of CF_2-I is quite low (ca. 200 kJ/mol),[19] the formation of diadduct $\mathbf{n_2}$ is favored over that of $\mathbf{n_1}$. In fact, the former contains two strong CF_2-CH_2 bonds (in the case of a tail addition), while the latter contains only one CF_2-CH_2 bond and a low energetic CF_2-I bond. $\mathbf{n_3}$ is much more difficult to form using that particular TFF/$I-R_F-I$ molar ratio, which does not allow a high propagation rate of TFP.

^{19}F NMR spectra of the first three fractions are shown in Figures S4−S6 (SI). The weak signals (7.4%) centered at −67.1 ppm corresponded to "reverse head addition" (i.e., $CF_2CH(CF_3)CH_2I$). The main peaks at −70.3 ppm (92.6%) were attributed to CF_3 adjacent to iodine end-atoms in the case of a "normal tail addition" (i.e., $CF_2CH_2CH(CF_3)I$). In the reactions of fluoroolefins, steric factors are of lesser importance because of the relatively small size of the fluoro substituent. In these circumstances, it should be expected that polar factors could play a role in determining regiospecificity. Application of the usual rules to TFP leads to a prediction that, for nucleophilic radicals (e.g., $t\text{-Bu}^\bullet$), the rate of head addition is enhanced (i.e., $t\text{-BuCH(CF}_3\text{)CH}_2^\bullet$). Similarly, for electrophilic radicals (perfluoroalkyl radicals in this present case), the rate of tail addition is favored. ^{1}H NMR spectra are displayed in Figures S7−S9 (SI). The doublet of quintets centered at 4.4 ppm was assigned to C*H of TFP and both multiplets at 3.0 and 2.7 ppm were attributed to CH_2 of TFP (AB system).

TFP telomers $\mathbf{n_2}$ were ethylenated by insertion of a 2.2-fold excess of ethylene, with *tert*-butyl peroxypivalate (TBPPi) as the radical initiator at 70 °C in *tert*-butyl alcohol, yielding **1** in 80% yield (Scheme 1, step 2). Telomer **1** was analyzed by GC (Figure S10, SI) then characterized by ^{19}F and ^{1}H NMR spectroscopies. The ^{19}F NMR spectrum (Figure S11, SI) is almost similar to that of $\mathbf{n_2}$ (Figure S5, SI). The ^{1}H NMR spectrum of **1** (Figure S12, SI) displayed signals at 3.2 and 2.1−2.25 ppm, which were assigned to CH_2I and CH_2CH_2I, respectively.

The hydrolysis of ethylenated TFP telomers **1** was carried out in step 3 (Scheme 1). Using DMF/H_2O at 120 °C has led to a mixture of diol **2** (35%) and alcohol-formiate **3** (65%). That was only evidenced by ^{1}H NMR (Figure S13, SI) and FTIR (Figure S14, SI), since the ^{19}F NMR spectrum (Figure S15, SI) is almost similar to that of **1** (Figure S11, SI). In Figure S13 (SI), the peak at 7.96 ppm was assigned to the OC*H*O formiate end-group. The CH_2OH end-group gave signals at 3.8 ppm, and CH_2O*H* appeared at 2.7 ppm. In Figure S14 (SI), the FTIR spectrum exhibited two characteristic bands: a broad strong one at 3650−3000 cm^{-1} characteristic of OH groups and a weak one at 1712 cm^{-1} corresponding to OCHO groups. Thus, an additional step 4 (Scheme 1) using sulfuric acid in methanol for 4 h has allowed converting alcohol-formiate **3** into diol **2** in 70% yield over two steps. This has been confirmed by ^{13}C NMR (Figures S16 before step 4 and S17 after step 4 (SI)). A signal at 160.5 ppm, related to OCHO, was observed only in Figure S16 (SI). Two quartets with negative intensities at 36.9−36.0 and 34.2−33.5 ppm with $^2J_{CF}$ = 28 Hz were assigned to C*H of TFP units. Both triplets at 29.8−29.4 and 28.8−27.6 ppm were attributed to CH_2 adjacent to TFP units with two possible structures: $R_FCH_2CH(CF_3)$− and $R_FCH(CF_3)CH_2$−. The triplet at 22.5 ppm ($^2J_{CF}$ = 28.9 Hz) was assigned to CH_2CF_2 fragments. ^{19}F NMR and ^{1}H NMR spectra for **2** are displayed in Figures S18 and S19 (SI), respectively.

Fluorinated diol **2** was obtained in 25% overall yield over four steps. The molecular weight of **2** was assessed by GPC that evidenced a M_n of 670 g/mol (using polystyrene standards) with a narrow PDI of 1.13. This fluorinated diol displayed good thermal stability. Its decomposition temperature at 10 wt % loss was 170 °C (Figure S20, SI). The DSC thermogram displayed a glass transition temperature at −56 °C (Figure S21, SI). Given that diols of type $HOC_2H_4C_6F_{12}C_2H_4OH$ are crystalline,[18a] the amorphous state of **2** is thus clearly linked to the insertion of TFP moieties.

The other two pathways dealt with the radical addition of $\mathbf{n_2}$ onto allyl alcohol or allyl acetate, initiated by AIBN at 90 °C (Scheme 2). The corresponding bis(iodohydrin) **4** and diiododiacetate **5** were selectively obtained in ca. 70% yield, yet avoiding byproducts bearing end-groups of types $CH_2CH(OH)CH_2I$ and $CH_2CH(OAc)CH_2I$, respectively.

^{19}F NMR spectra of **4** and **5** were identical (Figures S22 and S23 (SI), respectively). ^{1}H NMR spectra of **4** and **5** are presented in Figures S24 and S25 (SI), respectively. As compared to that of $\mathbf{n_2}$ (Figure S8, SI), new characteristic signals appeared as multiplets: one centered at 4.26 ppm assigned to C*(I)H, and that from 2.0 to 2.4 ppm belonging to the CH_2 flanked by two asymmetric carbons (AB system). In the case of diiododiacetate **5**, intensive signals at 2.05 ppm were assigned to CH_3 of acetates end-groups (Figure S25, SI).

A 3-fold excess of Bu_3SnH enabled the selective reduction[13c] of **4** and **5** under vigorous stirring leading to **7** and **6** in 44% and 63% yield, respectively. The unreacted tributyltin hydride was reacted with potassium fluoride in diethyl ether at room temperature for 3 h. Telomer **6** was hydrolyzed by H_2SO_4/MeOH at room temperature for 4 h leading to fluorinated telechelic diol **7** in 65% yield. Diol **7** was obtained in ca. 13% overall yield via both pathways (over three steps via the allyl alcohol pathway and over four steps through the allyl acetate route). ^{19}F NMR spectra for **7** and **6** are displayed in Figures S26 and S27 (SI), respectively. As expected, the reduction of iodine did not trigger much change in the signals attributed to CF_3 and C_6F_{12}. However, the ^{1}H NMR spectrum of **7** (Figure S28, SI) displayed upfield shifts comparing to those observed for **4** and **5** (Figures S24 and S25 (SI), respectively). In addition, the signal centered at 4.4 ppm assigned to C***H**(I) disappeared in the ^{1}H NMR spectrum of **7**. ^{13}C NMR spectrum for **7** (Figure S29, SI) is almost similar to that for **2** (Figure S17, SI).

The hydrolysis of the acetates **6** into hydroxyl groups was monitored by FTIR (Figure S30, SI), which showed the increase of the broad band at 3410 cm^{-1}, while that at 1527 cm^{-1} (assigned to carbonyl frequency of acetates) vanished versus time. GPC chromatograms displayed narrow molecular distribution with PDI values lower than 1.3 (Figures S31 and S32, SI). TGA thermograms are shown in Figures S33 and S34 (SI). The decomposition temperatures at 2, 10, and 50% weight loss were observed at 70, 125, and 200 °C, respectively. From the DSC thermogram (Figure S35, SI), **7** exhibited a very low glass transition temperature at ca. −65 °C.

In summary, this work describes facile strategies for the syntheses of original fluorinated diols containing 3,3,3-trifluoropropene (TFP) moieties. The first common step of all pathways involved the radical telomerization of TFP with 1,6-diiodoperfluorohexane initiated by di-*tert*-butyl peroxide. This reaction afforded α,ω-bis(TFP) telomers in ca. 80% yield. Mono-, di-, and triadducts were isolated by distillation. Through the first pathway, the $I(TFP)R_F(TFP)I$ diadduct was end-capped at both sides by ethylene under radical conditions leading to the corresponding diiodinated telechelic in 80% yield. Then, a two-step process led to the corresponding α,ω-fluorinated diol in 25% overall yield. The other strategies, which dealt with the radical addition of $I(TFP)R_F(TFP)I$ diadduct onto allyl acetate or allyl alcohol using AIBN as the radical initiator, have led to the corresponding iodinated adducts in ca. 70% yield. A subsequent reaction of reduction of iodine atoms gave rise to the corresponding diol and diacetate in 44% and 63% yield, respectively. The latter was easily hydrolyzed into diol, thus leading to original telechelics in 13% overall yield. All the telomers were characterized by NMR spectroscopies. The fluorinated diols displayed satisfactory thermal stabilities with a decomposition temperature at 10 wt % loss ranging from 125 to 170 °C. They also exhibited very low glass transition temperature of ca. −60 °C along with narrow molecular weight distributions. Further work on the condensation of such diols to prepare polyesters and bis-cyclocarbonates via telechelic diepoxides is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data (^{1}H, ^{13}C, and ^{19}F NMR and FTIR spectra; TGA and DSC thermograms; GPC or SEC chromatograms). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Great Lakes (now Chemtura) Co. (USA) for sponsoring this work and for kindly providing TFP. Solvay and AkzoNobel are also acknowledged for supplying 1,1,1,3,3-pentafluorobutane and *tert*-butyl peroxypivalate, respectively.

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