Synthesis and Radical Polymerization of 1,1-Difluoro-2-vinylcyclopropane: A Reexamination and Structural Reassignment

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ABSTRACT: The synthesis and radical polymerization of 1,1-difluoro-2-vinylcyclopropane, first reported some 30 years ago, has been repeated and the assignment of polymer structure examined in detail. The monomer and polymer have been characterized by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy, differential scanning calorimetry, and size exclusion chromatography. Analysis of the data establishes that the earlier assignments by Zhulin et al. were erroneous, and the reassignment is in agreement with expectations based on Dolbier's theoretical and experimental examination of radical ring opening of fluorinated cyclopropanes.

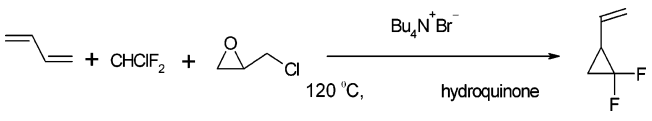
Introduction

In a program directed to the preparation of electrostrictive materials, we seek routes to polar polymers with glass transition temperatures (T_gs) below room temperature. We have described routes based on the ring-opening metathesis polymerization and copolymerization of fluorinated monomers followed by hydrogenation;[1] an alternative approach involves the radical ring-opening polymerization (RROP) of substituted vinylcyclopropane (VCP) monomers carrying polar groups on the cyclopropyl ring.[2] The monomer 1,1-difluoro-2-vinylcyclopropane is not expected to give a low-T_g polymer by this route, but it is a model for a family of substituted vinylcyclopropanes which are potentially suitable monomers for the synthesis of low-T_g polymers; consequently, we have synthesized and polymerized this monomer. Detailed NMR characterization of both the monomer and the polymer establishes that earlier assignments were erroneous and provides evidence in support of Dolbier's more recent studies of the course of ring opening of fluorinated cyclopropanes.[3]

Results and Discussion

(a) Synthesis and Characterization of 1,1-Difluoro-2-vinylcyclopropane. A convenient route to 1,1-difluoro-2-vinylcyclopropane is the addition of difluorocarbene to 1,3-butadiene. Difluorocarbene can be generated in many ways;[4−10] for our purposes we adopted the route initially reported by Buddrus,[4] which generates difluorocarbene from chlorodifluoromethane at 120 °C in epichlorohydrin in the presence of tetrabutylammonium bromide and hydroquinone (Scheme 1).

Scheme 1. Synthesis of 1,1-Difluoro-2-vinylcyclopropane



Although this route requires fairly drastic reaction conditions, the recovery and purification of the product is simpler than alternative routes, and the hazards associated with volatile mercury compounds[8] and the requirement for a multistep reagent synthesis[9] are avoided. Chlorofluorocarbons and epichlorohydrin are both environmentally hazardous, but the former is degraded during reaction and the latter can be disposed of safely by standard laboratory practice. We obtained 1,1-difluoro-2-vinylcyclopropane in 30% yield with a purity above 99% as assessed by capillary gas chromatography. Although known since 1967,[4] the detailed NMR spectroscopic proof of structure for this monomer has not been reported. The ^{1}H NMR spectrum is shown in Figure 1. The shifts and integrations are entirely consistent with the assigned structure and, taken with the gas chromatography result, demonstrate that the monomer is pure; although it is, of course, a racemic mixture. The numbering system system used for NMR assignments is shown in Figure 2. The vinyl hydrogens are assigned on the basis of the values of the J^3_{HH} coupling constants, 10.4 Hz (cis), 17.1 Hz (trans), and the ∼1.4 Hz vicinal HH coupling. A COSY spectrum allowed identification of H_4, leaving only an ambiguity concerning the assignment of H_5 and H_6 to be resolved (see Figure 2).

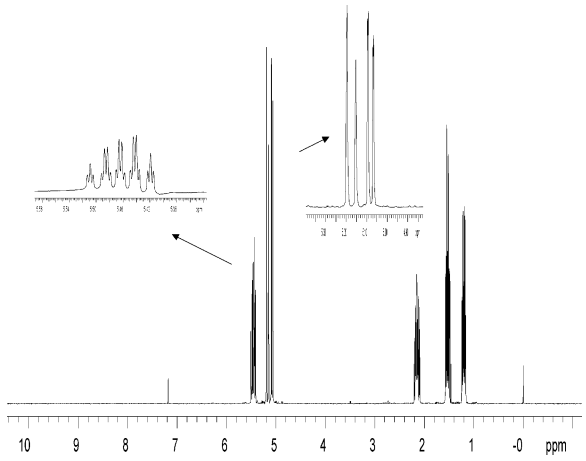


Figure 1. ^{1}H NMR spectrum of 1,1-difluoro-2-vinylcyclopropane.

In the ^{19}F NMR spectrum, the difluoromethylene shows a J_{FF} coupling of 155.8 Hz, which is in the expected range for a cyclopropyl CF_2. The signal at −141.61 ppm is assigned as F_7 on the basis of the observed splitting, a triplet (J^3_{HF} = 13.0 Hz) of doublets (J^3_{HF} = 4.2 Hz), while the signal at −128.62 ppm (F_8) appears as a doublet (J^3_{HF} = 13.2 Hz) of doublets (J^3_{HF} = 5.2 Hz) of doublets (J^3_{HF} = 0.8 Hz). In both signals the larger

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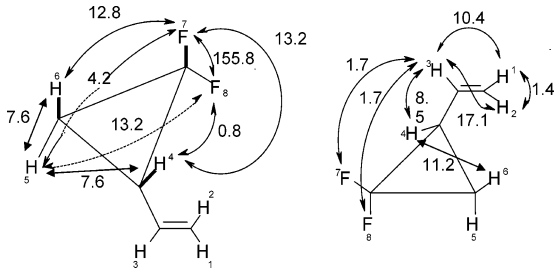
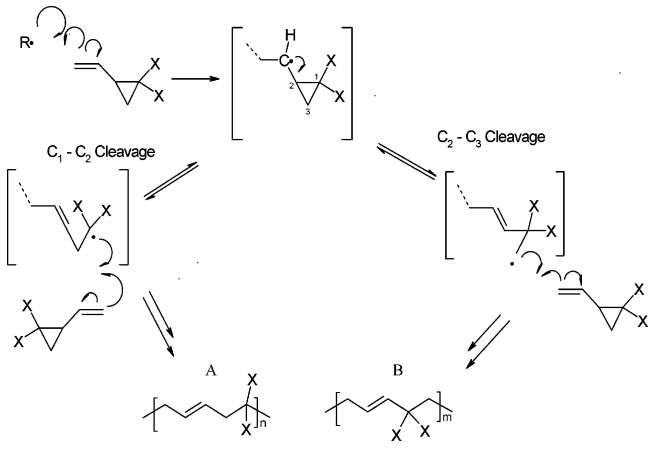


Figure 2. Observed coupling constants of 1,1-difluoro-2-vinylcyclopropane.

Scheme 2. General RROP Mechanism of the Disubstituted VCP Monomers



splitting has a value which is in the normal range for a three-bond syn HF coupling in a cyclopropyl, and the smaller splittings are consistent with a three-bond anti HF coupling. The assigned coupling constants in hertz are shown in Figure 2.

In the ^{13}C NMR spectrum the CF_2 carbon appears at 113.5 ppm as a doublet of doublets, $J^1_{C-F} = 287.6$ and 284.6 Hz, due to the slightly different fluorine environments. The J^1_{C-F} values are in the normal range expected for the fluorine-substituted carbons of a cyclopropyl.[11] The two other carbons in the ring occur at lower frequency, the ring carbon substituted with the vinyl group at 26.7 ppm displays a doublet of doublets ($J^2_{C-F} = 12.3$ and 11.6 Hz), and the unsubstituted carbon appears at 12.7 ppm as a triplet ($J^2_{C-F} = 10.8$ Hz). The methine carbon of the vinyl group at 131.5 ppm displays a doublet of doublets ($J^3_{C-F} = 4.6$ and 1.5 Hz), and the methylene vinyl carbon is seen as a singlet at 117.6 ppm. Taken together, these spectroscopic data confirm the assigned structure.

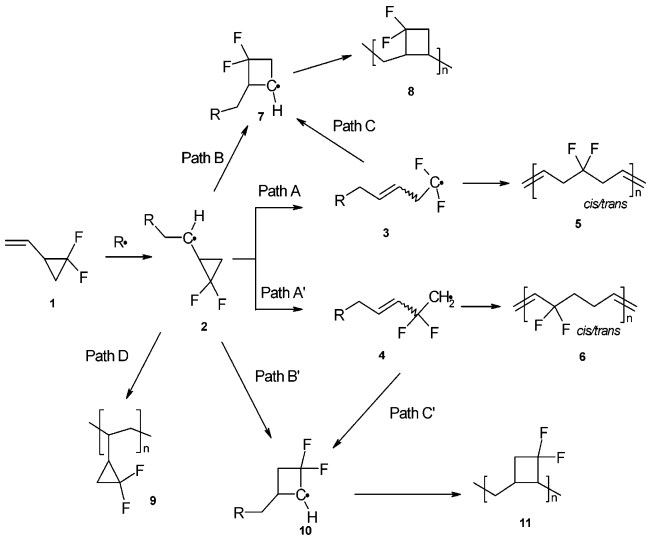
(b) Radical Ring-Opening Polymerization of 1,1-Difluoro-2-vinylcyclopropane. The generally accepted mechanism for the RROP of VCP monomers is shown in Scheme 2.[12] Radical attack on the least hindered vinyl carbon gives a cyclopropylcarbinyl radical that rearranges to an allyl carbinyl radical with, predominantly, a trans double bond; this intermediate initiates chain growth via the same sequence of steps. Most of the reported RROPs of disubstituted VCPs lead to polymers resulting from breaking of the C_1-C_2 bond in the intermediate cyclopropylcarbinyl radical; this is described as 1,5-addition polymerization and is shown on the left-hand side of Scheme 2, leading to polymers of structure A. The highest conversions and molecular weights are reported for monomers containing cyano and/or carboxy substituents. These observations are consistent with the radical stabilizing and/or the electron-withdrawing effects of the substituents in increasing the susceptibility to radical polymerization and influencing the direction of ring opening.

The ring-opening polymerization of 1,1-difluoro-2-vinylcyclopropane has been reported to follow predominantly the pathway established for chlorine-, cyano-, and carboxy-substituted monomers; it was claimed that radically initiated polymerization at room temperature gave a polymer having structure A (Scheme 2, X = F, 91 ± 1%) and structure B as the minor component (9 ± 1%); no T_g or molecular weight data were reported for the polymer.[7] The RROP of 1,1-difluoro-2-vinylcyclopropane was repeated as part of a larger program of work[13] because, although a low-T_g polar elastomer was unlikely to be obtained, the monomer synthesis and polymerization would provide useful characterization data and reference points for the larger study; additionally, there were theoretical considerations (see below) which cast doubt on the validity of the structural assignments in the earlier report. The assignment of structures in the earlier work was based on an analysis of ^{19}F NMR and IR spectra. The fluorine atoms in structures A and B (Scheme 2, X = F) have different environments consistent with the two signals seen in the ^{19}F NMR spectrum. The spectrum shown in the earlier publication,[7] which is reasonably consistent with the one obtained in the present work, displays two signals of unequal relative intensity; the major signal at −94.1 ppm was assigned to the fluorine atoms in structure A and the signal at −90.5 ppm to the minor structure B. These assignments were based on the assumption that the double bond reduces the screening of fluorine nuclei in the α-position; consequently, the fluorines in the CF_2 in structure B should appear downfield with respect to the signal due to the fluorines in structure A. The assumptions concerning the screening effects of the double bond on difluoromethylene groups were based on the observed ^{19}F NMR spectra of perfluorocyclopentene, which is an inappropriate model for this purpose, and so these assignments cannot be regarded as secure.

The analysis of the IR spectrum led Zhulin et al.[7] to postulate that the absence, in the polymer spectrum, of bands at 1020 cm^{-1} (skeletal vibrations of a three-membered ring) and 3090 cm^{-1} (bond stretching vibrations of CH_2 in the ring) observed in the spectrum of the monomer and the appearance of a strong band at 1680 cm^{-1} (double bond stretching) indicated that only the structures A and B in Scheme 2 were present in the polymer backbone. Further, since −CH═CH− stretching is usually relatively weak in symmetrically substituted double bonds, they assumed that the double bond stretching associated with structure A was too weak to detect and that the band observed at 1680 cm^{-1} in the polymer spectrum, which was relatively strong, involved a double bond vibration with a dipole moment change consistent with the minor isomer, i.e., structure B. This argument, depending on "relative strengths" of bands, is also insecure in the absence of appropriate reference compounds. In a related study Dolbier et al.[3] predicted that fluorine substitution in a cyclopropane ring produces a dramatic impact on behavior with respect to radical ring opening. These predictions are based on a theoretical study using density functional theory calculations which revealed a lower energy barrier for the ring opening of the difluorocyclopropylcarbinyl radical via C_2-C_3 cleavage, than for the C_1-C_2 ring opening; i.e., Dolbier's work implies that the right-hand side of Scheme 2 should be favored in this specific case, which contradicts the earlier assignment.

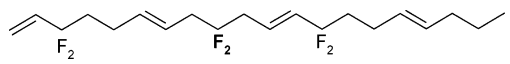
The polymerization of neat 1,1-difluoro-2-vinylcyclopropane was carried out in an oxygen-free atmosphere using AIBN (0.75 mol %) as radical initiator. The colorless liquid was stirred at 50 °C for 5 days, becoming viscous by the end of the process. The benzene-soluble product was recovered as a white powder

Scheme 3. Possible Structures for the Product of RROP of 1,1-Difluoro-2-vinylcyclopropane

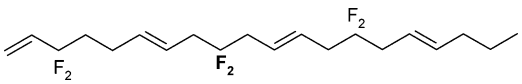


in low yield (15%) by precipitation into cold methanol. The possible structures for the radically initiated polymerization 1,1-difluoro-2-vinylcyclopropane system are shown in Scheme 3.[14−17] In the ^{19}F NMR spectrum of the product (see Figure 3), the major signal (91%) is seen at −96.11 ppm. This is a fairly broad signal in which a 12.4 Hz splitting can be seen and has an adjacent low-intensity multiplet at −96.36 ppm. The other signal with significant intensity occurs at −92.02 ppm (9%) and appears as a quartet (J = 15.4 Hz); this peak also has an adjacent low-intensity multiplet at −91.8 ppm. Two other small peaks are seen at −87.7 and −88.2 ppm (∼0.4%). As will emerge from our analysis of the ^{13}C and ^{1}H spectra of the polymer, the major structural feature (91%) is assigned to structure **6** (Scheme 3) and the minor structural feature to structure **5**.

The other low-intensity peaks in the ^{19}F NMR spectrum might be indicative of minor contributions of structures such as **8**, **9**, and **11** (Scheme 3); however, the cyclopropyl unit (**9**) can be ruled out as it would be expected in the region −120 to −150 ppm, and the cyclobutane units (**8** and **11**) also seem unlikely on the basis of the observed chemical shifts.[11] The very small signals adjacent to the main signals are probably due to sequence effects in the distribution of repeat units. For an all-trans vinylene polymer, the repeat units are either symmetrical (S, minor) or unsymmetrical (U, major). If the incorporation is statistical, the most probable situation for the minor repeat unit is in the sequence USU; that is, we assign the signal at −92.02 ppm to the following structure:



The adjacent occurrence of a pair of S units has a probability of 0.01 if the incorporation is statistical, and the minor peak at −91.8 ppm is about 1/10th of the intensity of the peak at −92.02 ppm (itself ca. 10% of the total ^{19}F intensity) and can be assigned to the following USS sequence:



On this basis it would appear that the incorporation of the two different repeat units is statistical. A similar analysis cannot be applied to the larger peak with its adjacent peak because of

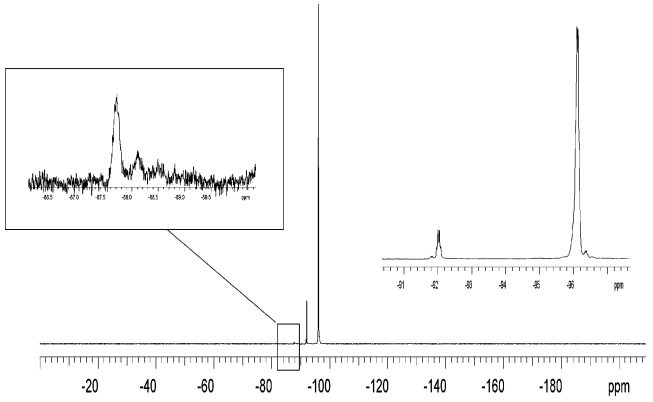


Figure 3. ^{19}F NMR spectrum of poly(1,1-difluoro-2-vinylcyclopropane).

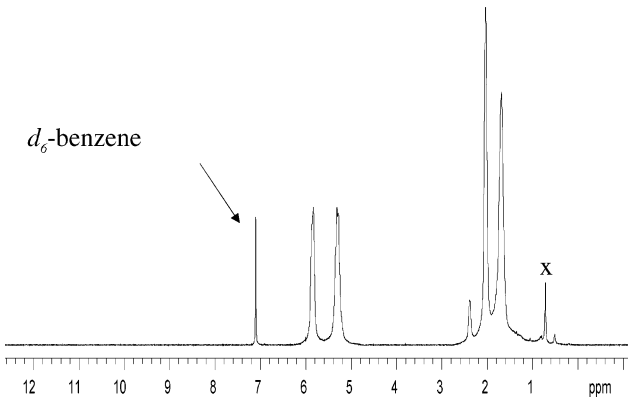


Figure 4. ^{1}H NMR spectrum of poly(1,1-difluoro-2-vinylcyclopropane); x indicates solvent impurity.

overlapped signals. The very small peaks at −87.7 and −88.2 ppm remain unassigned and may be structural defects arising from dehydrofluorination or chain ends or regioinversion of the unsymmetrical repeat units. Thus, the current ^{19}F NMR spectrum of this polymer is in broad agreement with that reported in the earlier work,[7] apart from a discrepancy of about 2 ppm in the chemical shift and the extra low-intensity signals identified in this work. The differences can be attributed to improvements in equipment during the past 30 years and different referencing procedures.

In the ^{1}H NMR spectrum shown in Figure 4 the bulk of the signal intensity is contained in four major peaks, which are all fairly broad. These are two vinylic signals and two methylene signals, and this is only consistent with structure **6** in Scheme 3 being the major structural feature, since only the unsymmetrical repeat unit generates these four different environments for the hydrogens. The two signals observed in the vinyl region have different intensity, and this suggests a possible overlapping with the signal from the vinylene hydrogens in the symmetrical structure **5** shown in Scheme 3. The signal at 5.2 ppm possesses a higher relative intensity; the difference in intensity between these vinylic signals leads to a major:minor structural composition ratio of 88:12 compared to the ratio 91:9 obtained from the analysis of the ^{19}F NMR spectrum, which is within the experimental error of the method since no check was carried out to ensure that the ^{19}F spectra were entirely quantitative. The smaller signal at 2.44 ppm was assigned to the allylic hydrogens in the symmetrical structure **5**, but the overlapping with neighboring signals does not allow an accurate integration. The narrow lines at ca. 0.5 (trace water) and 0.7 ppm (probably hexane) are contaminants.

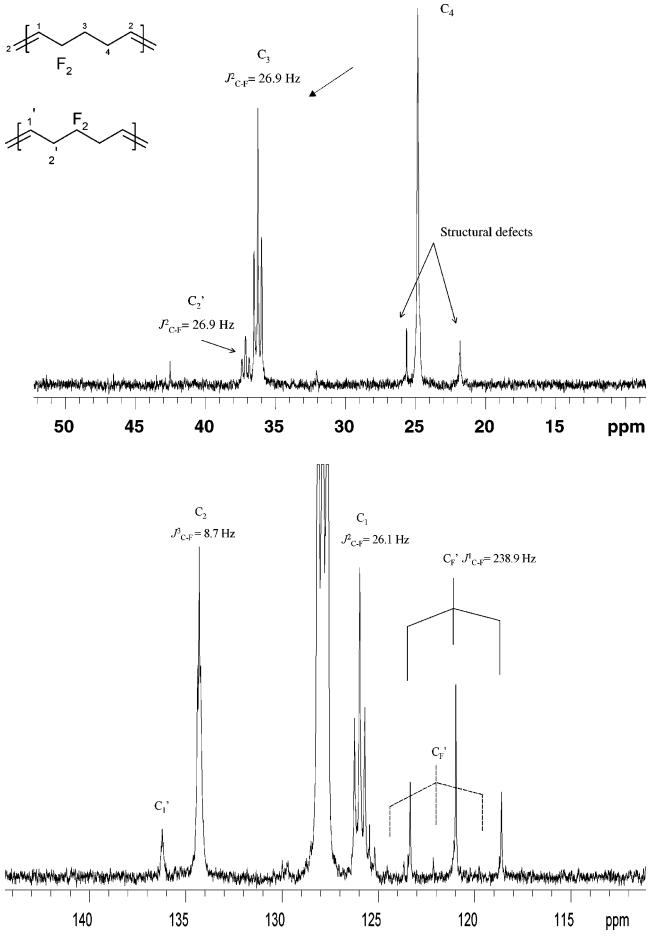


Figure 5. ^{13}C NMR spectrum of of poly(1,1-difluoro-2-vinylcyclopropane); unsaturated region (above) and vinyl region (below).

Analysis of the ^{13}C NMR spectrum was conclusive in assigning the major structural features of the polymer. In the spectrum, Figure 5, four major and a minor signal are observed. The minor triplet signal at 120.99 ppm ($J^1_{C-F} = 238.9$ Hz) arises from the CF_2 unit. Two major signals are observed in the vinyl region at 125.9 and 134.3 ppm; both are resolved into triplets and therefore coupled with the CF_2. The different coupling constants, respectively $J^2_{C-F} = 26.1$ Hz and $J^3_{C-F} = 8.7$ Hz, are only consistent with the unsymmetrical repeat unit, and the observed coupling constants are in the expected range.[11] The methylene region of the spectrum shows two major signals, which again is only consistent with an unsymmetrical repeat unit; one of them is a triplet $J^2_{C-F} = 26.9$ Hz at 36.2 ppm, and the other repeat unit is a singlet at 24.86 ppm. The signal of the methylene carbons of the symmetrical repeat unit (**5**) appears at 37.1 ppm as triplet with a $J^2_{C-F} = 27.0$ Hz, the signal for the vinyl carbons in this minor structure is found as a broad multiplet at 136.22 ppm, and the signals associated with the CF_2 carbon appear as a very weak triplet at 122.1 ppm ($J^1_{C-F} = 239$ Hz).

The relative simplicity of the NMR spectra implies that the vinylenes are all cis or trans but does not allow an assignment. The nature of the double bonds in the polymer structure was determined by IR spectroscopy (not shown here). A band at 971 cm^{-1} is characteristic of the out-of-plane bending mode for the C−H of trans double bonds, whereas the characteristic band for the cis double bonds, expected between 730 and 675 cm^{-1}, does not appear. The absorption band for −CH═CH− stretching appears at 1684 cm^{-1} in agreement with earlier work,[7] in a relatively low intensity, which is normal in trans double bonds. The C−F stretching vibration appears as a sharp strong band in the IR spectrum in the fingerprint region at 1384 cm^{-1}.

The polymer displays a T_g of 55.6 °C (DSC), and GPC analysis gave $M_w = 59\,600$ and $M_n = 33\,500$, with a PDI = 1.78 vs polystyrene calibration. This molecular weight obtained is higher than those from RROP of VCP monomers bearing chloride or bromide groups ($M_w \sim 1000$);[18] however, it is substantially lower than values reported for RROP of VCP monomers bearing ester or cyano groups ($M_w > 100\,000$).[19] The TGA analysis indicated that less than 0.5% of the mass is lost at 300 °C (10 °C/min, in N_2), which indicates a relatively high stability for this fluorinated polymer. The elemental analysis was consistent with the assigned structure.

Experimental Section

General Considerations. Dry solvents were obtained using a purpose built purifying system. A Braun nitrogen glovebox operating at <1 ppm water and oxygen was used when required. AIBN was recrystallized twice from methanol and dried under vacuum. Butadiene (Aldrich, 99+% pure), manipulated by vacuum transfer, was dried and deoxygenated, and inhibitors were removed prior to use. Other reagents were used as supplied.

Infrared spectra were recorded between KBr disks using a Nicolet NEXUS FTIR spectrometer. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded using Varian Mercury-400 and Inova-500 NMR spectrometers. The solvents used were deuterated chloroform for monomer spectra and deuterated benzene for polymer spectra; ^1H and ^{13}C NMR spectra were referenced to TMS and ^{19}F spectra to $CFCl_3$ via the ^2H frequency of the solvent. Gas chromatography (GC) was recorded using a Hewlett-Packard (HP) 5890 series II fitted with a HP5 nonpolar (5% diphenyl, 95% dimethylsiloxane) capillary column; starting oven temperature 40 °C, ramp 10 °C min^{-1} to 300 °C; flame ionization detector. Gel permeation chromatography (GPC) was carried out using a Knauer HPLC pump (model 64), a Waters model R401 differential refractometer detector, and three Plgel columns with pore sizes of 10^2, 10^3, and 10^5 Å. The sample solutions were filtered through a Whatman WTP type 0.2 μm filter before injection onto the column. The columns were calibrated using Polymer Laboratories polystyrene standards.

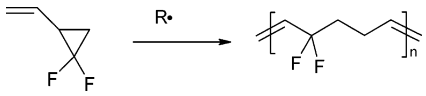
Synthesis of 1,1-Difluoro-2-vinylcyclopropane. 1,3-Butadiene (11 g, 200 mmol) and $CHClF_2$ (26 g, 300 mmol) were vacuum transferred into a steel vessel containing 3-chloroepoxypropane (28 mL, 360 mmol), Bu_4NBr (0.2 g, 0.6 mmol), and hydroquinone (0.04 g, 0.34 mmol). The vessel was sealed under vacuum and heated at 120 °C for 10 h. The contents of the vessel were fractionally distilled (Vigreux column, 20 cm × 1 cm) to give 1,1-difluoro-2-vinylcyclopropane (6.45 g, 30% yield) as a colorless liquid (bp 52−53 °C, literature[4] 51.5−52 °C) (>99.9% purity by capillary GC, t_R = 5.45 min). ^1H NMR (δ ppm): 5.54 (1H, dddt, J^3_{H-H}(trans) = 17.1 Hz, J^3_{H-H}(cis) = 10.4 Hz, J^3_{H-H} = 8.5 Hz, J^4_{H-F} = 1.7 Hz, CH═CH_2 [H_3]); 5.25 (1H, dd, J^3_{H-H} = 17.1 Hz, J^2_{H-H} = 1.4 Hz, CH_2═C−H [H_2]); 5.16 (1H, dd, J^3_{H-H} = 10.4 Hz, J^2_{H-H} = 1.4 Hz, cis CH_2═C−H [H_1]); 2.23 (1H, dddd, J^3_{H-F}(syn) = 13.2 Hz, J^3_{H-H}(syn) = 11.2 Hz, J^3_{H-H}(anti) = 7.6 Hz, J^3_{H-H} = 8.5 Hz, J^3_{H-F}(anti) = 0.8 Hz, CH−CH═CH_2 [H_4]); 1.61 (1H, dddd, J^3_{H-F}(syn) = 12.8 Hz, J^3_{H-H}(syn) = 11.2 Hz, J^2_{H-H} = 7.6 Hz, J^3_{F-H}(anti) = 5.2 Hz, CH_2-ring [H_6]); 1.28 (1H, dtd, J^3_{H-F}(syn) = 13.2 Hz, J^3_{H-H}(anti) = 7.6 Hz, J^2_{H-H} = 7.6 Hz CH_2-ring [H_5]). ^{19}F NMR (δ ppm): −128.62 (1F, dtd, J^2_{F-F} = 155.8 Hz, J^3_{F-H}(syn) = 12.8 Hz, J^3_{F-H}(syn) = 13.2 Hz, J^3_{F-H}(anti) = 4.2 Hz [F_7]); −141.65 (1F, ddd, J^2_{F-F} = 155.86 Hz, J^3_{F-H}(syn) = 13.2 Hz, J^3_{F-H}(anti) = 0.8 Hz). ^{13}C NMR (δ ppm): 131.5 (dd, J^2_{C-F} = 4.6, and 1.5 Hz, = CH−); 117.6 (s, H_2C═); 113.5 (dd, J^1_{C-F} = 287.6, and 284.6 Hz, C−F); 26.7 (dd, J^2_{C-F} = 12.3 and 11.6 Hz, CH ring); 12.7 (t, J^2_{C-F} = 10.8 Hz, CH_2 ring).

Polymerization of 1,1-Difluoro-2-vinylcyclopropane. Using the glovebox, the initiator AIBN (0.012 g, 0.07 mmol) was dissolved in the monomer (1 g, 9.6 mmol), and the resulting solution was transferred into an oxygen-free ampule equipped with Young's

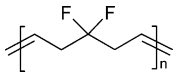
Teflon vacuum tap and a magnetic stirrer. The sealed ampule (nitrogen atmosphere) was taken out of the glovebox and heated with stirring at 50 °C for 5 days. The contents of the ampule were recovered by precipitation into a 10-fold excess of cold methanol to give a white solid. The product was recovered by filtration and dried in a vacuum oven at 50 °C overnight. The white solid was redissolved in the minimum quantity of benzene and reprecipitated using a 10-fold excess of methanol, recovered by filtration, and dried in the vacuum oven to give poly(1,1-difluoro-2-vinylcyclopropane) (0.15 g, 15%). Found: C, 58.04; H, 5.83; F, 36.0; $(C_5H_6F_2)_n$ requires C, 57.69; H, 5.77; F, 36.54%. ^{1}H NMR (δ/ppm, S symmetrical, U unsymmetrical): 5.6−6 (bs, U, ═C*H*−CF_2); 5−5.5 (bs, S and U, C*H*═ overlapped); 2.3−2.5 (bs, S, CH_2−CF_2); 1.8−2.3 (bs, U, CH_2−CF_2); 1.2−2.2 (bs, U, CH_2−CH═). ^{19}F NMR (δ/ppm, rel int (%) S symmetrical, U unsymmetrical): 87.7 (bm, <0.5); 88.2 (m, <0.5); 91.8 (q, <0.5); 92.02 (q, S, J^3_{H-F} = 15.43 Hz, 8.8); 96.11 (q, U, J^3_{H-F} = 12.4 Hz, 90.8); 96.36 (m, <0.5). ^{13}C NMR (δ/ppm, S symmetrical, U unsymmetrical): 135.2 (bm, S, CH═); 134.3 (t, U, J^3_{C-F} = 8.7 Hz, *C*H═C−CF_2); 125.9 (t, U, J^2_{C-F} = 26.1 Hz, CH═*C*H−CF_2); 122.1 (t, S, J^1_{C-F} = 239 Hz, CF_2); 120.99 (t, U, J^1_{C-F} = 238.9 Hz, CF_2); 37.1 (t, S, J^2_{C-F} = 27 Hz, *C*H_2−CF_2); 36.26 (t, U, J^2_{C-F} = 26.9 Hz, *C*H_2−CF_2); 24.86 (s, U, *C*H_2−CH═).

Conclusions

The assignments reported here for the structure of poly(1,1-difluoro-2-vinylcyclopropane) are in agreement with predictions based on the theoretical calculations reported by Dolbier et al.[3] and are in disagreement with the structure reported previously by Zhulin et al.[7] This work establishes that the RROP of 1,1-difluoro-2-vinylcyclopropane proceeds mainly via cleavage of the C−C bond opposite the CF_2 unit in the ring to give mainly (ca. 90%) the following unsymmetrical repeat unit:



The symmetrical structure constitutes ca. 10% of the polymer structure, and detailed analysis of the ^{19}F NMR spectrum leads to the conclusion that the repeat units are statistically incorporated.



The adopted synthesis works and is a potentially useful route to a novel fluoropolymer, but the material obtained is not appropriate for the requirements of this electrostrictive elastomer project as the T_g is above room temperature. Attempts to modify the monomer structure via incorporation of an *n*-alkyl chain in order to induce T_g lowering internal plasticization were unsuccessful.

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References and Notes

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