

# An Extraordinarily Rapid Polymerization of Vinylpentafluorocyclopropane: Highly Stereo- and Regioselective Synthesis of Unsaturated Fluoropolymers†

Zhen-Yu Yang\*

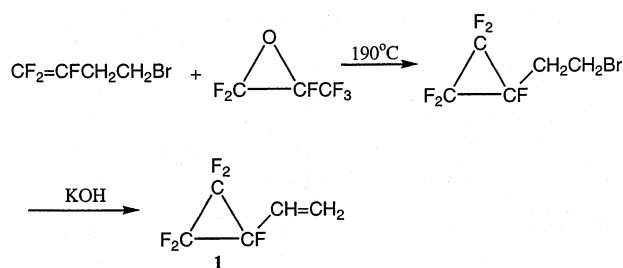
DuPont Central Research and Development, Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

Received October 21, 2002; E-mail: Zhenyu.yang-1@usa.dupont.com

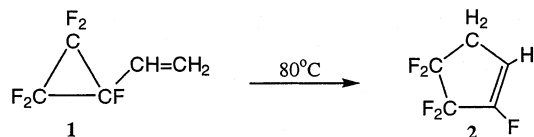
Fluoropolymers, particularly saturated fluoropolymers, have excellent thermal and chemical stability, low surface energy, high insulating ability, and low refractive index and dielectric constant, but their limited solubility and high crystallinity necessitate extreme processing conditions.<sup>1</sup> Nonfluorinated polymers containing double bonds are useful materials which can be further modified by cross-linking or grafting to improve properties. These materials can be readily prepared by radical polymerization of 1,3-dienes. However, perfluorobutadiene does not polymerize to give a high-molecular weight polymer with radical initiators, although anion-catalyzed polymerization was reported recently.<sup>2,3</sup> Radical polymerization of fluoromonomers to make fluoropolymers containing double bonds is very important since the fluorinated double bonds are highly polarized and can be used as electrophilic centers for cross-linking or grafting.<sup>4</sup> The polarized double bonds of fluoropolymers are usually generated by base elimination of hydrofluoride from vinylidene fluoride-based polymers; however, this process is constrained by the limited diffusion of dehydrofluorination agents through these polymers and the generation of harmful volatiles.<sup>5</sup> Other fluoropolymers are extremely resistant to double bond generation due to their high stability.<sup>6</sup> I have designed and synthesized the monomer vinylpentafluorocyclopropane **1** to produce polymers with polarized double bonds that are not accessible through radical polymerization of fluorinated dienes or dehydrofluorination of other fluoropolymers.

The polymerization of nonfluorinated vinylcyclopropanes is well documented, and the polymer structures obtained are dependent on the polymerization conditions. With cationic initiators, vinylcyclopropane gave a polymer with predominantly 1,2-structure units, resulting from polymerization of the double bond.<sup>7</sup> However, under radical conditions vinylcyclopropanes mainly gave ring-opened polymers with double bonds in backbones.<sup>8</sup> That is due to the fact that the rate of ring-opening of a cyclopropylcarbinyl radical is very fast ( $10^8 \text{ s}^{-1}$ ).<sup>9</sup> Introduction of two fluorines to a cyclopropyl carbinyl radical further facilitates the ring-opening reaction in 3 orders of magnitude, because the fluorine substituents affect both the structure and reactivity of cyclopropane.<sup>10</sup> One would expect vinylpentafluorocyclopropane **1** to be even more reactive to polymerization under radical conditions due to the high strain energy in perfluorinated cyclopropane systems. Synthesis of **1** is straightforward from the low cost and commercially available starting material  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Br}$ . Reaction of  $\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{Br}$  with hexafluoropropylene oxide at 190 °C gave the fluorinated cyclopropane derivative in 82–90% yield.<sup>11</sup> Elimination of HBr was accomplished by treatment with KOH in ethanol and water to form the desired monomer **1** in 92% yield.

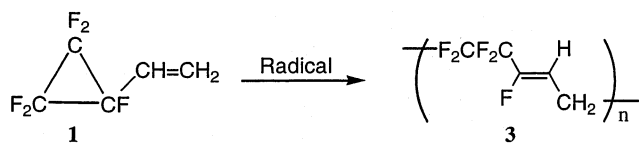
Monomer **1** is a low-boiling (bp 30 °C) liquid. It is stable at low temperature, having been stored at –40 °C for more than seven years without decomposition, but it polymerized to give a white



solid while standing at room temperature for a few hours. When heated to 80 °C or above, compound **1** was readily isomerized to give **2** in high yield ( $E_a = 28.7 \text{ kcal/mol}$ ).<sup>12</sup> In contrast, rearrangement of nonfluorinated vinylcyclopropanes to cyclopentenes required much higher temperatures ( $E_a = 49.7\text{--}51.7 \text{ kcal/mol}$ ),<sup>13</sup> while introduction of *gem*-difluorines to cyclopropane facilitated the rearrangement reaction to give difluorocyclopentene ( $E_a = 41.5 \text{ kcal/mol}$ ).<sup>14</sup>



When monomer **1** was treated with bis(perfluoropropionyl) peroxide (3P) in 1,1,2-trichlorotrifluoroethane at 40 °C, rapid polymerization occurred to form a white solid in greater than 90% yield. The polymer is insoluble in common organic solvents such as acetone, ethyl acetate, acetonitrile, THF, DMF, hexafluorobenzene, and other fluorocarbon solvents at room temperature, so that its molecular weight could not be measured by GPC.

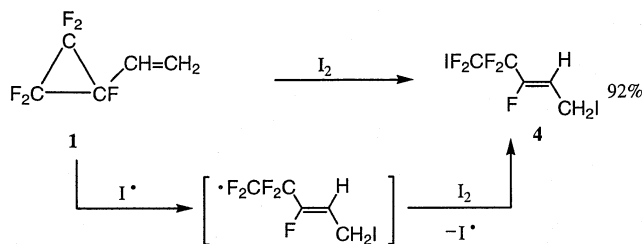


Polymerization of nonfluorinated vinylcyclopropanes gave amorphous polymers with both *cis* and *trans* double bonds as well as cyclobutyl rings.<sup>8</sup> In contrast, monomer **1** rapidly polymerizes with surprisingly high stereoselectivity and regioselectivity. Only 1,5-ring polymerization and *Z*-double bond conformations were observed. The polymer microstructure was characterized by FTIR and multinuclear NMR. The absorption of the double bond ( $1719 \text{ cm}^{-1}$ ) was observed by IR. <sup>1</sup>H and <sup>19</sup>F NMR analyses were obtained on the molten polymer at 135 °C. The <sup>1</sup>H NMR spectrum revealed a doublet of triplets for the vinyl hydrogen at 5.84 ppm, with a coupling constant for the doublet of 31.2 Hz, indicating a *trans* arrangement for the vinyl hydrogen and fluorine atoms. A multiplet

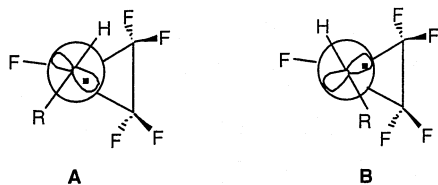
† Publication no.: 8346.

at 3.22 ppm corresponds to the methylene hydrogens.<sup>15</sup> <sup>19</sup>F NMR revealed the vinyl fluorine at -123.0 ppm and two sets of methylene fluorines -111.8 and -117.0 ppm, respectively. No fluorocyclobutyl structure was observed. The integration ratio was precisely consistent with the polymer structure formed via a clean ring-opening polymerization. The molecular weight ( $M_n$ ) of **3** made by 3P initiator and bis(4-*tert*-butylcyclohexylperoxy)dicarbonate was  $6.5 \times 10^4$  and  $7.5 \times 10^4$ , respectively, based on NMR end group analysis.

The *Z*-double bond configuration in **3** was further confirmed by chemical conversion. Under radical conditions, **1** reacted with iodine in  $\text{CH}_2\text{Cl}_2$  at 0 °C to room temperature to give the diiodide **4** in high yield. GC showed a single peak, and <sup>1</sup>H NMR analysis exhibited a doublet of triplets at 5.97 ppm with coupling constants of 30.1 and 9.0 Hz, respectively. The larger coupling is due to the trans F-H coupling, indicative of the *Z*-olefin.



The extraordinarily rapid polymerization of **1** may be attributed to the high strain of the pentafluorocyclopropyl ring and the favorable polar transition state between an electron-deficient pentafluorocyclopropyl ring and a relatively electron-rich double bond. The high *Z*-stereoselectivity of the double bonds in polymer **3** and the diiodide **4** could be rationalized by the favored transition state **A** for the ring-opening of a pentafluorocyclopropylcarbinyl radical to a *Z*-allyl radical rather than the disfavored transition state **B**, which experiences a steric repulsion between the bulky R group with the pentafluorocyclopropyl group.<sup>16</sup>



The regiospecific polymerization is due, at least in part, to the rigidity of the fluorocarbon chain and the lack of cyclization to four-membered rings which are common in nonfluorinated systems.<sup>8</sup> In addition, the propagation rate is faster than that of the hydrocarbon counterpart due to the favorable polarity match-ups in the transition state for addition of a fluorinated radical to a hydrocarbon double bond.<sup>17</sup>

TGA and DSC were used to evaluate the thermal characteristics of the homopolymer **3**. TGA (20 °C/min) revealed that, despite its unsaturation, polymer **3** has good thermal stability with a 10% weight loss temperature of about 400 °C in  $\text{N}_2$  and 375 °C in air. DSC analysis of **3** displayed a melting transition at 130 °C with no detectable glass transition above room temperature. In contrast to amorphous polymers from nonfluorinated vinylcyclopropanes, the high crystallinity of **3** is probably a result of segments packing regularly due to the fact that **3** has highly uniform steric structures. **3** can readily be pressed into a tough and clear thin film at 150 to 180 °C.

The monomer **1** also copolymerizes with other fluorinated monomers, such as tetrafluoroethylene, chlorotrifluoroethylene, and perfluoropropyl vinyl ether. All of the copolymers had good thermal

stability and exhibited 10% weight losses above 400 °C in  $\text{N}_2$ . DSC showed that the copolymers were highly crystalline, but their melting points were only a few degrees different from that of the homopolymer, indicating incorporation of only small amounts of these comonomers.<sup>18</sup>

**Acknowledgment.** I thank Mr. R. E. Smith, Jr. for technical assistance and Dr. M. Hofmann for his comments.

**Supporting Information Available:** Experimental procedures for **1**, **2**, **3**, **4** and a copolymer and characterization data for all compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Wall, L. A., Ed. *Fluoropolymers*; John Wiley & Sons: New York, 1972; Vol. XXV. (b) Scheirs, J., Ed. *Modern Fluoropolymers*; John Wiley & Sons: New York, 1997.
- (2) Toy, M. S.; Lawson, D. D. *J. Polym. Sci., Polym. Lett. Ed.* **1968**, *6*, 639. Toy, M. S.; Newman, J. M. *J. Polym. Sci., Part A-1* **1969**, *7*, 2333.
- (3) Narita, T.; Hagiwara, T.; Hanana, H.; Sezaki, M.; Nagai, A.; Nishimura, S.; Takahashi, A. *Macromolecules* **1989**, *22*, 3183. Narita, T.; Hagiwara, T.; Hanana, H.; Sezaki, M.; Nagai, A.; Nishimura, S.; Takahashi, A. *Makromol. Chem.* **1991**, *192*, 351.
- (4) Ameduri, B.; Boutevin, B.; Kostov, G. *Prog. Polym. Sci.* **2001**, *26*, 105. Logothetis, A. *Prog. Polym. Sci.* **1989**, *14*, 251.
- (5) Schmiegel, W. W. *Angew. Makromol. Chem.* **1979**, *76*, 39. Fogiel, A. W. *J. Polym. Sci. Symp.* **1975**, *53*, 333.
- (6) Most highly fluorinated polymers are stable to various bases. For example, strong bases have no effect on copolymers of ethylene with tetrafluoroethylene (ETFE). Perfluoropolymers are more stable to bases than partially fluorinated polymers. Carlson, D. P.; Schmiegel, W. *Ullmann's Encyclopedia of Industrial Chemistry*; VCH: Weinheim, 1988; Vol. A11, p 395.
- (7) Borchert, A. E.; Overberger, C. G. *J. Polym. Sci.* **1960**, *44*, 483. Overberger, C. G.; Borchert, A. E.; Katchman, A. *J. Polym. Sci.* **1960**, *44*, 491.
- (8) Takahashi, T. *J. Polym. Sci., Part A-1* **1968**, *6*, 403. Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1992**, *25*, 6719. Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818. Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 5748. Sugiyama, J.; Ohashi, K.; Ueda, M. *Macromolecules* **1994**, *27*, 5543. Mizukami, S.; Kihara, N.; Endo, T. *J. Am. Chem. Soc.* **1994**, *116*, 6453. Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 1346. Sanda, F.; Murata, J.; Endo, T. *Macromolecules* **1997**, *30*, 160.
- (9) Nonhebel, D. C. *Chem. Soc. Rev.* **1993**, *347*. Bowry, V. W.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687. Martin-Esker, A. A.; Johnson, C. C.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **1994**, *116*, 9174. Newcomb, M.; Horner, J. H.; Emanuel, C. J. *J. Am. Chem. Soc.* **1997**, *119*, 7147. Newcomb, M.; Glenn, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 275.
- (10) Tian, F.; Bartberger, M. D.; Dolbier, W. R., Jr. *J. Org. Chem.* **1999**, *64*, 540.
- (11) Sargeant, P. B.; Krespan, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 415. Sargeant, P. B. *J. Org. Chem.* **1970**, *35*, 678. Chepik, S. D.; Petrov, V. A.; Galakhov, M. V.; Belen'kii, G. G.; Mysov, E. I.; German, L. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, *8*, 1844.
- (12) Kinetic data for rearrangement of **1** to **2** are:  $\Delta G^\ddagger = 28.7$  kcal/mol,  $\Delta H^\ddagger = 26.7$  kcal/mol, and  $\Delta S^\ddagger = -5.5$  eu (log A = 12.7,  $E_a = 28.4$  kcal/mol). see Smart, B. E.; Kusic, P. J.; Roe, d. C.; Yang, Z. Y. *J. Fluorine Chem.* **2002**, *117*, 199.
- (13) (a) Flowers, M. C.; Frey, H. M. *J. Chem. Soc.* **1961** 3547. (b) Wellington, C. A., *J. Phys. Chem.* **1962**, *66*, 1671. (c) Retzlaff, D. G.; Coull, B. M. *J. Phys. Chem.* **1970**, *74*, 2455. (d) Lewis, D. K.; Charney, D. J.; Kalra, B. L.; Plate, A. M.; Woodward, M. H.; Cianciosi, S. J.; Baldwin, J. E. *J. Phys. Chem. A* **1997**, *101*, 4097.
- (14) (a) Dolbier, W. R., Jr.; Sader, B. H. A.; Sellers, S. F.; Koroniak, H. *J. Am. Chem. Soc.* **1981**, *103*, 2138. (b) Dolbier, W. R., Jr.; Sellers, S. F. *J. Am. Chem. Soc.* **1982**, *104*, 2494.
- (15) A small multiplet was observed at 6.05 ppm. This probably corresponds to the *cis*-vinyl hydrogen. The ratio of the peak at 5.84 ppm to the peak at 6.05 ppm is 14 to 1.
- (16) The ring-opening of a nonfluorinated cyclopropyl carbinyl radical does not have high stereo- and regiospecificity. See: Marino, P. S.; Bay, E. *J. Org. Chem.* **1980**, *45*, 1763. Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1473. Ratier, M.; Pereyre, M.; Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1907. Fluorine substituents have remarkable effects on stereo- and regiospecificity. Ring-opening of *gem*-difluorocyclopropylcarbinyl radical gave *E*-olefins. See: Morikawa, T.; Uejima, M.; Kobayashi, Y. *Chem. Lett.* **1988**, 1410. Morikawa, T.; Uejima, M.; Yoda, K.; Taguchi, T. *Chem. Lett.* **1990**, 467. The high strain energy of perfluorocyclopropyl further enhances the stereoselectivity of ring-opening due to much better interaction between the SOMO of the radical and the  $\sigma^*$  orbital of the perfluorocyclopropyl illustrated in the most favored transition state.
- (17) Dolbier, W. R., Jr. *Chem. Rev.* **1996**, *96*, 1557. Dolbier, W. R., Jr.; Li, A.; Smart, B. E.; Yang, Z. Y. *J. Org. Chem.* **1998**, *63*, 5687.
- (18) Yang, Z. Y. U.S. Patent 5,420,367, 1995.

JA021289I