

Articles

Structure-Property Relationship of Fluorinated Dioxole Polymers¹⁻³

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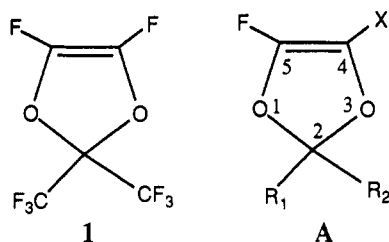
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ABSTRACT: Teflon-AF, based on the perfluoro-2,2-dimethyl-1,3-dioxole monomer (1), is a new class of high- T_g amorphous fluoroplastics with enhanced properties over traditional fluoropolymers. New monomer and polymer chemistry that relates to fluorodioxole molecules was explored. Synthetic methods for introducing different substituents at 2-, 4-, and 5-positions of the dioxole ring were developed. The structure-property relationships of these polymers were studied, and we have found that the polymer glass transition temperatures are highly sensitive toward the structure of these monomers. The results indicated that the steric bulkiness of the substituents on the dioxole ring is critical for polymer properties, not only in the determination of glass transition temperature but also on the rate of polymerization. A rationalization is proposed to explain these observations.

Introduction

Teflon-AF,⁴ a new fluoropolymer, was recently developed by DuPont. This material is a family of amorphous copolymers of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (1)⁵ and tetrafluoroethylene. These polymers are

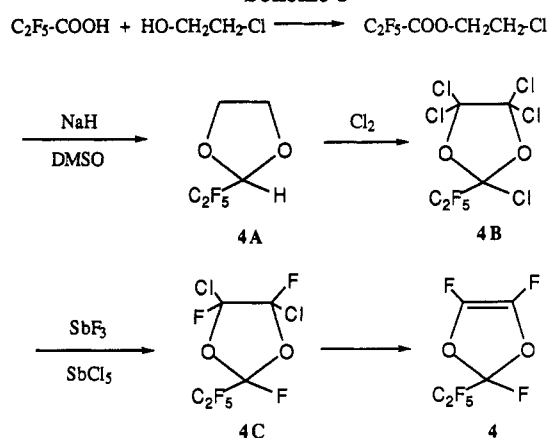


very similar to poly(tetrafluoroethylene) in chemical and thermal stability but have enhanced physical and mechanical properties, better optical clarity, and lower dielectric constants. In addition, they are soluble in selected fluorinated solvents, thus allowing the preparation of thin cast films.⁶ These unique characteristics make fluorodioxole polymers candidates for advanced electronic, optical, and biomedical applications.

The homopolymer of 1 exhibits a T_g at 330 °C, which is one of the highest among amorphous plastics. One explanation for the high glass transition temperature of dioxole homopolymer is the highly congested chain structure resulting from the two trifluoromethyl groups. If this hypothesis is true, the glass transition temperature of the dioxole polymer will be highly sensitive toward substituents on the dioxole ring. Indeed, in the copolymers of 1 with tetrafluoroethylene (TFE), T_g 's drop rapidly as the percentage of TFE increases. In this paper we report our studies about the relationship of polymer T_g to the structure of the fluorinated dioxole monomers, mainly through variations of substituent groups on the 2-, 4-, and 5-positions of the dioxole ring.

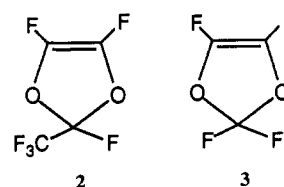
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Scheme I



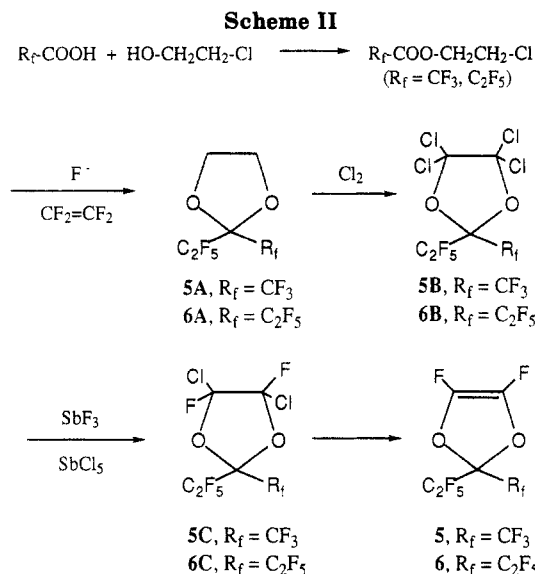
Results and Discussion

Initially, we investigated perfluorodioxoles with different fluoroalkyl groups at the 2-position. The syntheses of perfluoro-2-methyl-1,3-dioxole (PMD; 2)⁷ and perfluoro-1,3-dioxole (PD; 3)⁸ were previously reported. These two



monomers homopolymerize and copolymerize with TFE readily in 1,1,2-trichloro-1,2,2-trifluoroethane (F113) solvent with radical initiators at 50–70 °C. The homopolymers of 2 and 3 exhibit T_g 's at 212 and at 180 °C, respectively.

By comparing the glass transition temperatures of homopolymers 2 and 3 with that of 1, it seems reasonable to predict that the T_g 's of the perfluoro-1,3-dioxole polymer



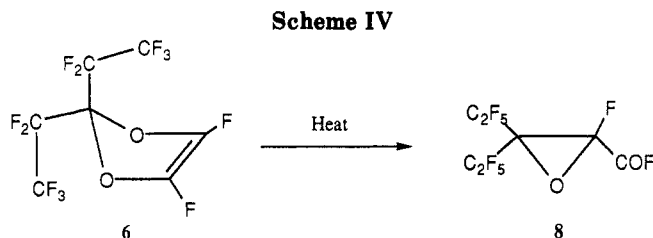
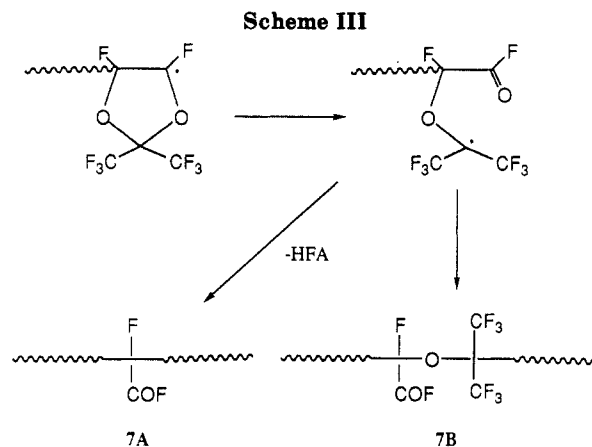
series will increase with the increasing bulkiness of the fluoroalkyl group at the 2-position of the dioxole ring.

To support this proposal, we have synthesized perfluoro-2-ethyl-1,3-dioxole (PED; 4) from 2-chloroethyl pentafluoropropionate⁹ (Scheme I). PED homopolymerizes about as well as 1 in terms of rate and polymer yield. However, the predicted trend for glass transition temperature did not hold; a single T_g at 150 °C was observed for PED homopolymer. Copolymerization of PED and TFE gave good yields of polymers, but the T_g 's of the copolymers are also substantially lower than the corresponding PMD/TFE or PD/TFE copolymers that possess similar compositions.

The T_g drop in PED polymers, compared to PMD and PD polymers, may be attributed to a pendant group effect. A perfluoroethyl group could have a larger free volume than either a trifluoromethyl group or a fluorine atom; this phenomenon was previously observed in the series of poly(ethyl acrylate) and poly(methyl acrylate).¹⁰

The study was extended to perfluoro-2-ethyl-2-methyl-1,3-dioxole (PEMD; 5), which was synthesized from tetrafluoroethylene/metal fluoride and 2-chloroethyl trifluoroacetate in four steps (Scheme II). Monomer 5 homopolymerizes much slower than 1. Interestingly, the resulting homopolymer does not exhibit a constant glass transition temperature. Instead, a range of 118–139 °C was observed for the polymers prepared under the same experimental conditions. One additional unusual observation was that the PEMD/TFE copolymers display higher than calculated average T_g values (a T_g plateau) between the 85/15 PEMD/TFE and 80/20 PEMD/TFE (mol %) copolymer compositions. This phenomenon was not found in the T_g -composition relationship curves of other fluorodioxole/TFE copolymers (Figures 1 and 2).

These unexpected results brought up the question of whether these fluorodioxole homopolymers have real homopolymer structures with all 1,3-dioxolane repeating units in polymer chains and contain no other structure. We have detected the formation of a small amount of hexafluoroacetone (HFA) during the polymerization of 1. Formation of HFA was presumably derived from the opening of the dioxolane ring as depicted in Scheme III. Placing a larger perfluoroethyl group in addition to the existing trifluoromethyl group at the 2-position of the monomer molecule may exert two effects. First, it increases ring strain, and second, it decreases the polymerization rate. Both effects should promote the ring-opening process.



As ring-opening occurs, the C–O bond is broken to reduce the steric strain between perfluoroalkyl groups, which are either within the same monomer unit or between neighboring units. The resulting polymeric radical intermediate could either keep propagating (7B) or first lose an HFA fragment before continuation of chain growth (7A). Both pathways would lower the steric congestion of perfluoroalkyl groups in the polymer chain and hence lower the polymer T_g . Since the amount of ring opening during the polymerization process was not controllable, T_g 's of the final polymers could vary somewhat rather than reach a constant value when the degree of ring opening reaches a certain level. In the case of PEMD/TFE copolymers, it seems that when the TFE content is higher than 20 mol %, the steric interaction may be small enough to prevent further ring openings. A T_g plateau could be the combined result of the above factors.

We also examined the monomer perfluoro-2,2-diethyl-1,3-dioxole (PDED; 6), synthesized in a way similar to Scheme II. We have found that PDED was very sluggish in either homopolymerization or copolymerizations with TFE. No polymer was obtained even under harsh conditions (rapid heating to 200 °C in a sealed tube in the presence of an initiator); only the monomer rearrangement product, epoxy acid fluoride 8,^{3a} was formed and isolated in good yields (Scheme IV). The relative inertness of PDED compared to PEMD toward polymerization apparently resulted from the "steric" factor, since electronically it would be very difficult to explain why the subtle difference in electronegativity between CF_3 and C_2F_5 groups will cause so different a behavior in polymerization.

The size of the pentafluoroethyl group is probably large enough (CF_3 is about the size of an isopropyl group) to cause serious steric and dipole–dipole interactions even within the PDED molecule. These C_2F_5 groups will try to stay apart from each other. Consequently, the C_2F_5 groups would bend back on the top and bottom faces of the molecule in a stable conformation and can well block the approach of other monomer units or polymer chains, thus strongly retarding the chain growth.

As described above, PDED will rearrange to epoxy acid fluoride 8 at high temperature. Under the same conditions, monomer PEMD (5) also partly converts to polymer and

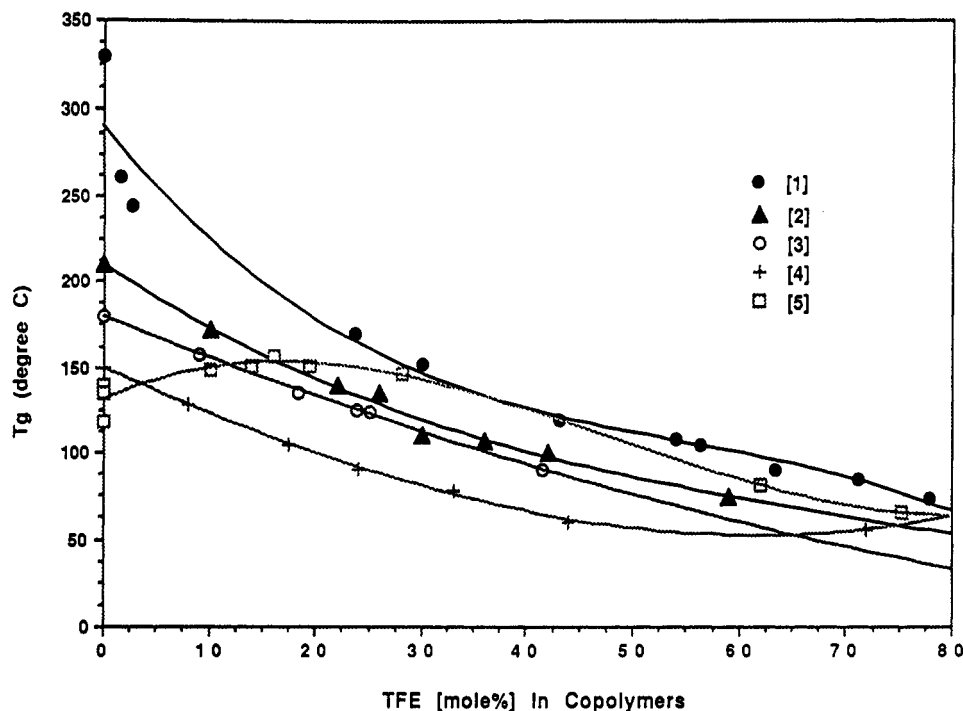


Figure 1. Relationship of glass transition temperature (T_g) and composition of the fluorodioxole polymers from monomers 1-5.

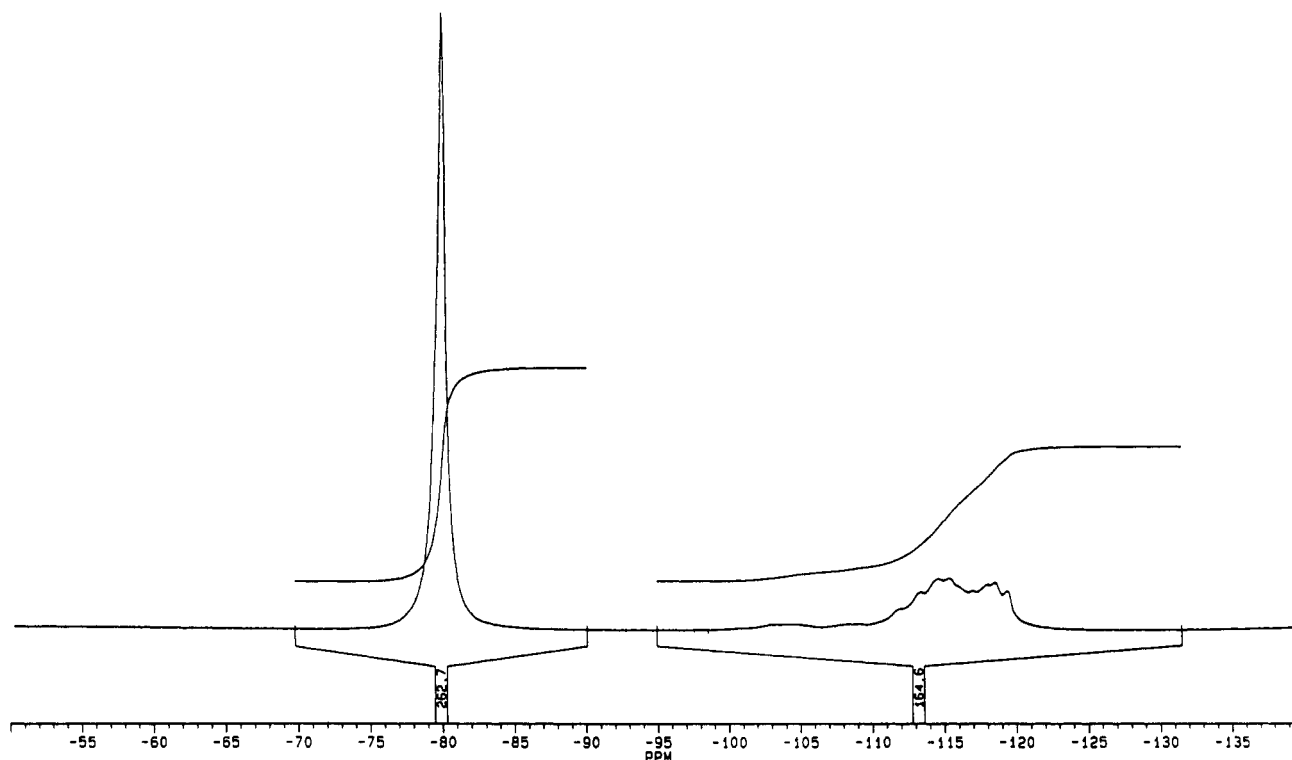
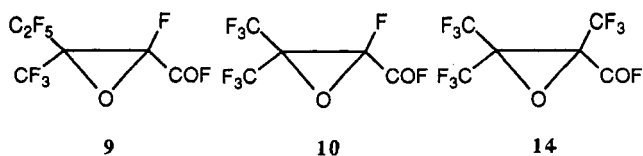


Figure 2. Representative ^{19}F high-temperature melt NMR spectrum of 1/TFE copolymer.

partly rearranges to the corresponding epoxy acid fluoride **9**.^{3c} In contrast, monomer **1** polymerizes rapidly rather



than rearranges when heated up quickly. Nevertheless, the corresponding epoxy acid fluoride **10**^{3a} from **1** could be formed in the gas phase at well above 200 °C. The relatively easy rearrangement for PDED and PEMD compared to **1** provides strong evidence that the sluggish

polymerization rate of PDED is caused by steric bulkiness. The release of ring strain eventually becomes the major driving force for the rearrangement process.

To determine suitable groups to attach to the 2-position of the dioxole ring, so that they are large enough to induce the desired high T_g but not hinder the polymerization, we have prepared another monomer, 2-(chlorodifluoromethyl)-2-(trifluoromethyl)-4,5-difluoro-1,3-dioxole (CTD; **11**) from chloropentafluoroacetone in a process similar to that of **1**.³ CTD was quite reactive to homopolymerization and afforded a white polymer with a T_g at 330 °C. This finding suggested that the ideal substituent size at the 2-position of the ring that would offer high T_g polymers

may be between CF_2Cl and C_2F_5 groups and plus a CF_3 group.

The steric effect at the 4- and 5-positions of the dioxole molecules was also investigated. We have found that the impact of substituent group sizes at these positions on the polymer T_g was also substantial. If one of the fluorines in 1 is replaced by hydrogen, T_g of the resulting homopolymer drops from 330 to 256 °C, as indicated in the case of 2,2-bis(trifluoromethyl)-4-fluoro-1,3-dioxole (12).¹¹

On the other hand, when one of the fluorines in 1 was replaced by a trifluoromethyl group, polymerization of this new monomer was totally retarded, as observed in the case of perfluoro-2,2,4-trimethyl-1,3-dioxole (PTD; 13).^{3a} Following the same reaction pattern as PDED (6), PTD rearranged to the corresponding epoxy acid fluoride 14 (but not epoxy ketone)^{3a} at high temperature without polymer formation. PTD also failed to copolymerize with TFE.

Replacing fluorine with chlorine in 1 as in the monomer 2,2-bis(trifluoromethyl)-4-chloro-5-fluoro-1,3-dioxole (15)¹¹ resulted in the formation of a low molecular weight homooligomer. Copolymerization of 15 with TFE proceeded at a reasonable rate, presumably due to the smaller size of chlorine compared to a trifluoromethyl group.

In conclusion, our studies revealed that the steric bulkiness of the substituent groups on the fluorodioxole monomers has very important influences on the glass transition temperature of the resulting polymers. Judging from the current experimental results, it seems reasonable that the best choices for a high- T_g fluorodioxole polymer are fluorine atoms on the 4- and 5-positions and two trifluoromethyl groups or one trifluoromethyl and one chlorodifluoromethyl group on the 2-position.

Experimental Section

¹H NMR spectra were recorded with a GEQE plus instrument at 300 MHz with CDCl_3 as the solvent and Me_4Si as the internal standard. The ¹⁹F NMR spectra were measured with a NIC 1180E instrument at 188.24 MHz and are reported in ppm upfield from CFCl_3 , which also served as the internal standard.

Monomers 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole (1),⁵ perfluoro-2-methyl-1,3-dioxole (PMD; 2),⁷ perfluoro-1,3-dioxole (PD; 3),⁸ 2,2-bis(trifluoromethyl)-4-fluoro-1,3-dioxole (12),¹¹ perfluoro-2,2,4-trimethyl-1,3-dioxole (PTD; 13),^{3a} and bis(trifluoromethyl)-4-chloro-5-fluoro-1,3-dioxole (15)¹¹ were prepared according to the published procedures. All monomers were stored in a -80 °F freezer before polymerization.

The compositions of the copolymers were determined by ¹⁹F NMR spectroscopy at temperatures higher than the T_g 's of the copolymers to ensure good resolution of the peaks for integration.

2-Chloroethyl Trifluoroacetate. A 1-L, round-bottomed flask equipped with a mechanical stirrer, an addition funnel, and a thermocouple was charged with trifluoroacetic acid (228 g, 2.0 mol) and concentrated sulfuric acid (150 mL). This mixture was cooled to 10 °C and 2-chloroethanol (169.1 g, 2.10 mol) was added dropwise through the addition funnel, while the pot was kept at 10–15 °C in an ice water bath. After the addition was complete, the reaction mixture was allowed to stir overnight at room temperature. The organic layer was separated and washed three times with a saturated NaHCO_3 aqueous solution, dried over magnesium sulfate, and distilled to give the product in 80–82% yield. Bp: 117–118 °C. ¹H NMR (300 MHz, CDCl_3): δ 4.56 (t, $J = 6$ Hz, 2H), 3.71 (t, $J = 6$ Hz, 2H). ¹⁹F NMR (188.24 MHz, CFCl_3): δ -75.7 (s). Anal. Calcd for $\text{C}_4\text{H}_6\text{F}_3\text{ClO}_2$: C, 27.28; H, 2.29. Found: C, 27.18; H, 2.19.

2-Chloroethyl Pentafluoropropionate. The same procedure as for the preparation of 2-chloroethyl trifluoroacetate was applied, except that pentafluoropropionic acid was used instead of trifluoroacetic acid. The yields were in the range of 65–81%. Pure 2-chloroethyl pentafluoropropionate is a clear colorless oil. Bp: 125–126 °C. ¹H NMR (300 MHz, CDCl_3): δ 4.51 (t, $J = 6$ Hz, 2H), 3.67 (t, $J = 6$ Hz, 2H). ¹⁹F NMR (188.24 MHz, CFCl_3):

δ -84.0 (s, 3F), -122.3 (s, 2F). Anal. Calcd for $\text{C}_5\text{H}_4\text{F}_5\text{ClO}_2$: C, 26.51; H, 1.78. Found: C, 26.14; H, 1.88.

Synthesis of Perfluoro-2-ethyl-1,3-dioxole (PED; 4). I. 2-(Pentafluoroethyl)-1,3-dioxolane¹² (4A). NaH (50% oil suspension; 28.8 g, 0.6 mol) was stirred in dried methyl sulfoxide (420 mL) at 15–20 °C. 2-Chloroethyl pentafluoropropionate (135.9 g, 0.6 mol) was added dropwise. After the addition was completed, the mixture was allowed to stir overnight at room temperature. The volatile material was distilled at 90 °C (6–8 mmHg). Further fractional distillation afforded the title product as a clear, colorless liquid. Bp: 95–97 °C. ¹H NMR (300 MHz, CDCl_3): δ 5.48 (t, $J = 8.7$ Hz, 1H), 4.13 (s, 4H). ¹⁹F NMR (188.24 MHz, CFCl_3): δ -83.0 (s, 3F), -131.3 (d, $J = 8.5$ Hz, 2F). Anal. Calcd for $\text{C}_5\text{H}_4\text{F}_5\text{O}_2$: C, 31.26; H, 2.62. Found: C, 31.67; H, 2.50.

II. 2-(Pentafluoroethyl)-2,4,4,5,5-pentachloro-1,3-dioxolane (4B). Compound 4A (neat) was photochlorinated under a GE Sun-Lamp at about 120 °C with chlorine. The reaction was monitored by gas chromatography and stopped when the conversion was completed. The product was purified by distillation. Compound 4b was isolated as a clear liquid. Bp: 75–76 °C (20 mm). Yield: 56–78%. ¹⁹F NMR (188.24 MHz, CFCl_3): δ -82.6 (s, 3F), -121.5 (s, 2F). Anal. Calcd for $\text{C}_5\text{Cl}_5\text{F}_5\text{O}_2$: C, 16.48; F, 26.07. Found: C, 16.91; F, 25.71.

III. 2-(Pentafluoroethyl)-4,5-dichloro-2,4,5-trifluoro-1,3-dioxolane (4C). Compound 4B (45 g, 0.124 mol) was added in small portions into premixed antimony pentachloride (40.4 g, 0.135 mol) and antimony trifluoride (89.4 g, 0.50 mol). After addition, the mixture was heated slowly to 110–120 °C with vigorous stirring. The reaction was monitored by gas chromatography and stopped when the conversion was completed. The volatile product was distilled out under vacuum, washed with a saturated NaHCO_3 aqueous solution, and purified by a second distillation. Compound 4C was obtained as a clear liquid. Bp: 81–83 °C. Yield: 25 g (64%). This product is a mixture of stereoisomers. ¹⁹F NMR (188.24 MHz, CFCl_3): δ -82.2 (2s, 3F), -129.8 (s, 2F), -81.3 (4m, 1F), [-56.0 (m), -56.5 (t, $J = 3.4$ Hz) (major isomer); -66.5 (d, $J = 3.4$ Hz), -69.5 (dt, $J = 11.6$ Hz, 3.4 Hz) (minor isomer)] (2F total). Anal. Calcd for $\text{C}_5\text{Cl}_2\text{F}_8\text{O}_2$: C, 19.07; Cl, 22.51; F, 48.26. Found: C, 18.96; Cl, 22.15; F, 48.48.

IV. Perfluoro-2-ethyl-1,3-dioxole (PED; 4). A 300-mL flask was charged with lithium aluminum hydride (8.0 g, 0.211 mol) and dry THF (120 mL). To this suspension was introduced with external cooling titanium(IV) chloride (9.84 g, 0.052 mol). After addition, the mixed reagents were heated to reflux for 30 min. After cooling back to 30 °C, dioxolane 4C was added slowly via syringe and the rate of addition was controlled to keep the pot temperature at 25–35 °C. When the addition was completed, the mixture was stirred a further 10–15 min. Heat was then applied to distill out the volatile product. Monomer 4 was obtained as a clear liquid. Bp: 40 °C. Yield: 12.8 g (54%). ¹⁹F NMR (188.24 MHz, CFCl_3): δ -83.8 (d, $J = 8.0$ Hz, 3F), -130.8 (d, $J = 4.5$ Hz, 2F), -72.8 (m, 1F), -161.9 (d, $J = 4.5$ Hz, 2F). IR: 1894 cm^{-1} . Anal. Calcd for $\text{C}_5\text{F}_8\text{O}_2$: C, 24.59; F, 62.30. Found: C, 24.20; F, 61.95.

Synthesis of Perfluoro-2-ethyl-2-methyl-1,3-dioxole (PEMD; 5). I. 2-(Trifluoromethyl)-2-(pentafluoroethyl)-1,3-dioxolane¹² (5A). A 360-mL Hastelloy C shaker tube was charged with 2-chloroethyl trifluoroacetate (88.3 g, 0.5 mol), cesium fluoride (76 g, 0.5 mol), and a methyl sulfoxide solvent (100 mL). This tube was cooled in a dry ice/acetone bath and evacuated, and tetrafluoroethylene (TFE; 50 g, 0.5 mol) was transferred into the tube. This tube was sealed and agitated at 75 °C for 120 h. After cooling, the tube was vented to remove excess TFE. The reaction mixture was first filtered to remove any solid residue, and the filtrate was stirred in a 10% sodium hydroxide aqueous solution for 1 h. The organic layer was separated, washed three times with water, and then distilled on a spinning band column to give product 5A (52.5 g, 40%) as a clear colorless liquid. Bp: 55 °C (195 mm). ¹H NMR (300 MHz, CDCl_3): δ 4.28 (s). ¹⁹F NMR (188.24 MHz, CFCl_3): δ -80.3 (m, 3F), -82.2 (m, 3F), -125.0 (q, $J = 10.2$ Hz, 2F). Anal. Calcd for $\text{C}_6\text{H}_4\text{F}_8\text{O}_2$: C, 27.69; H, 1.55; F, 58.45. Found: C, 27.40; H, 1.48; F, 58.12.

II. 2-(Trifluoromethyl)-2-(pentafluoroethyl)-4,4,5,5-tetrachloro-1,3-dioxolane (5B). A 200-mL, three-neck, round-bottomed flask equipped with a thermocouple, a gas inlet tube,

and a dry ice condenser was charged with 5A (40 g, 0.154 mol). The reaction system was first purged with nitrogen, and the substrate was heated to 110 °C. At this temperature introduction of chlorine gas was started. In the meantime a GE Sun-Lamp was lit. The flow of chlorine gas and the heating power were adjusted so that the reaction temperature of the system was kept at 110–125 °C during the process.

The reaction was monitored by gas chromatography and stopped when the conversion was almost complete. The product was distilled under vacuum to yield the pure 5B as a clear colorless liquid. Bp: 64 °C (17 mm). Yield: 95%. ¹⁹F NMR (188.24 MHz, CFC1₃): δ -77.2 (m, 3F), -80.3 (m, 3F), -120.9 (q, J = 8.5 Hz, 2F). Anal. Calcd for C₆Cl₄F₈O₂: C, 18.11; Cl, 35.64; F, 38.20. Found: C, 17.97; Cl, 35.83; F, 38.07.

III. 2-(Trifluoromethyl)-2-(pentafluoroethyl)-4,5-dichloro-4,5-difluoro-1,3-dioxolane (5C). A 300-mL, round-bottomed flask was charged with compound 5B (60 g, 0.151 mol), antimony pentachloride (46.7 g, 0.156 mol), antimony trifluoride (74.5 g, 0.417 mol), and titanium tetrachloride (2.86 g, 0.015 mol). The whole reaction mixture was heated up to 100–110 °C with vigorous stirring. The reaction was allowed to proceed for 6–8 h, and then the volatile product was distilled out directly from the residual antimony salts under reduced pressure at 50 mm.

The distillate was washed with a saturated sodium bicarbonate aqueous solution and redistilled to give the pure product 5C as a clear colorless liquid. Bp: 42 °C (50 mm). The yields were in the range of 72–91%. This product is a mixture of trans/cis isomers. ¹⁹F NMR (188.24 MHz, CFC1₃): δ -80.2 (m, 3F), -81.3 (m, 3F), -124.5 (m, 2F), [-49.1 (m) (major isomer); -57.3 (q, J = 6.6 Hz) (minor isomer)] (2F total). Anal. Calcd for C₆-Cl₂F₁₀O₂: C, 19.75; Cl, 19.43; F, 52.06. Found: C, 20.13; Cl, 19.47; F, 51.75.

IV. Perfluoro-2-ethyl-2-methyl-2,3-dioxole (5). A 200-mL flask was charged with lithium aluminum hydride (6.14 g, 0.162 mol) and tetrahydrofuran (THF; 100 mL) under a nitrogen atmosphere. Titanium tetrachloride (7.67 g, 0.041 mol) was introduced into the flask gradually via a syringe with vigorous stirring; the pot was kept at 10–15 °C with external cooling. The color of the solution turned to black gradually with the addition of titanium tetrachloride. After finishing addition, the reagents were heated to reflux for 30 min and then cooled back to 30 °C. At this time, compound 5C (29.5 g, 0.081 mol) was added via syringe at a rate that kept the pot temperature at 25–35 °C. Some external cooling may be necessary.

When the introduction of the substrate was completed, the volatile product 5 was distilled out from the reaction mixture to an ice water chilled receiver. Bp: 42–43 °C. Yield: 40%. Small amounts of THF which codistilled out could be removed by washing the distillate with ice water. ¹⁹F NMR (188.24 MHz, CFC1₃): δ -81.9 (q, J = 4.5 Hz, 3F), -83.2 (m, 3F), -127.7 (m, 2F), -161.2 (s, 2F). IR: 1888 cm⁻¹. Anal. Calcd for C₆F₁₀O₂: C, 24.51; F, 64.41. Found: C, 24.38; F, 64.36.

Synthesis of Perfluoro-2,2-diethyl-1,3-dioxole (PDED; 6). The synthesis of monomer 6 was a sequence similar to the monomer 5 synthesis. The process was started from 2-chloroethyl pentafluoropropionate as shown in Scheme II.

I. 2,2-Bis(pentafluoroethyl)-1,3-dioxolane (6A). A 360 mL Hastelloy C shaker tube was charged with 2-chloroethyl pentafluoropropionate (113.3 g, 0.5 mol), cesium fluoride (76 g, 0.5 mol), and a methyl sulfoxide solvent (100 mL). The tube was cooled, evacuated, and charged with tetrafluoroethylene (TFE; 50 g, 0.5 mol). After shaking at 65 °C for 5 days, the tube was opened and the product was worked up similarly as described. Distillation yielded the desired product 6A (53 g, 34%) as a clear colorless liquid. Bp: 68–70 °C (140 mm). ¹H NMR (300 MHz, CDCl₃): δ 4.30 (s). ¹⁹F NMR (188.24 MHz, CFC1₃): δ -82.0 (m, br, 6F), -124.0 (m, br, 4F). Anal. Calcd for C₇H₄F₁₀O₂: C, 27.11; H, 1.30; F, 61.27. Found: C, 27.01; H, 1.24; F, 60.99.

II. 2,2-Bis(pentafluoroethyl)-4,4,5,5-tetrachloro-1,3-dioxolane (6B). This compound was prepared from 6a in the same way as described in the preparations of 4B and 5B, with yields in the range of 77–87%. Product 6B is a clear colorless liquid. Bp: 64 °C (10 mm). ¹⁹F NMR (188.24 MHz, CFC1₃): δ -79.7 (tm, J = 9.0 Hz, 6F), -119.8 (m, br, 4F). Anal. Calcd for C₇Cl₄F₁₀O₂: C, 18.77; Cl, 31.66; F, 42.42. Found: C, 18.65; Cl, 31.81; F, 42.25.

III. 2,2-Bis(pentafluoroethyl)-4,5-dichloro-4,5-difluoro-1,3-dioxolane (6C). This compound was prepared from 6B (48 g, 0.107 mol) with antimony pentachloride (33 g, 0.111 mol), antimony trifluoride (52.65 g, 0.295 mol), and titanium tetrachloride (2.03 g, 0.011 mol) at between 100 and 110 °C for 8 h. The volatile product was then distilled out directly from the reaction mixture at reduced pressure (50 mm), washed with a saturated sodium bicarbonate solution, and distilled again to afford the pure product as a clear liquid. Bp: 55 °C (40 mm). Yield: 82–89%. This product is a trans/cis isomeric mixture. ¹⁹F NMR (188.24 MHz, CFC1₃): δ -80.6 (m, br, 6F), -122.7 (m, br, 4F), [-47.6 (br) (major isomer), -55.5 (br) (minor isomer)] (2F total). Anal. Calcd for C₇Cl₂F₁₂O₂: C, 20.26; Cl, 17.09; F, 54.94. Found: C, 19.91; Cl, 17.48; F, 54.34.

IV. Perfluoro-2,2-diethyl-1,3-dioxole (6). This monomer was prepared from compound 6C by a dechlorination reaction using titanium tetrachloride/lithium aluminum hydride as the reagents. This reaction was carried out on a scale of 36 g (0.087 mol) of the precursor and used the same procedures as illustrated in the preparation of monomers 4 and 5. The pure product is a clear colorless oil. Bp: 52 °C. Yield: 44%. ¹⁹F NMR (188.24 MHz, CFC1₃): δ -82.3 (m, 6F), -127.3 (m, 4F), -162.8 (s, 2F). IR: 1895 cm⁻¹. Anal. Calcd for C₇F₁₂O₂: C, 24.42; F, 66.28. Found: C, 24.36; F, 65.90. Mass for [M]. Calcd: 343.9707. Found: 343.9724.

Synthesis of 2-(Chlorodifluoromethyl)-2-(trifluoromethyl)-4,5-difluoro-1,3-dioxole (CTD; 11). **I. 2-(Chlorodifluoromethyl)-2-(trifluoromethyl)-1,3-dioxolane.** A 210-mL shaker tube was charged with tetrabutylammonium bromide (0.25 g) and distilled water (0.2 mL). This tube was cooled and evacuated, and then ethylene oxide (12 g, 0.273 mol) and chloropentafluoroacetone (50 g, 0.274 mol) were transferred into the tube. The tube was sealed and heated at 80 °C for 1 h, at 100 °C for 1 h, and at 120 °C for 5 h. After cooling and unloading, the product mixture was purified by fractional distillation. The title compound was obtained as a clear liquid. Bp: 76–78 °C (100 mm). Yield: 20 g (32.3%). ¹H NMR (300 MHz, CDCl₃): δ 4.40 (s). ¹⁹F NMR (188.24 MHz, CFC1₃): δ -78.8 (t, J = 12 Hz, 3F), -66.0 (q, J = 12 Hz, 2F). Anal. Calcd for C₅H₂ClF₅O₂: C, 26.51; H, 1.78; Cl, 15.65; F, 41.93. Found: C, 26.37; H, 1.78; Cl, 15.54; F, 41.67.

II. 2-(Chlorodifluoromethyl)-2-(trifluoromethyl)-4,4,5,5-tetrachloro-1,3-dioxolane. This compound was prepared from 2-(chlorodifluoromethyl)-2-(trifluoromethyl)-1,3-dioxolane using the chlorination procedure described above. ¹⁹F NMR (188.24 MHz, CFC1₃): δ -74.5 (dt, J = 2 Hz, 11 Hz, 3F), -64.2 (dq, J = 2 Hz, 11 Hz, 2F). Bp: 78 °C (19 mm). Anal. Calcd for C₅-Cl₄F₅O₂: C, 16.48; Cl, 48.66; F, 26.07. Found: C, 16.39; Cl, 49.02; F, 25.69.

III. 2-(Chlorodifluoromethyl)-2-(trifluoromethyl)-4,5-dichloro-4,5-difluoro-1,3-dioxolane. This compound was prepared from 2-(chlorodifluoromethyl)-2-(trifluoromethyl)-4,4,5,5-tetrachloro-1,3-dioxolane with antimony pentachloride and antimony trifluoride in a similar procedure as described above. This product is a mixture of stereoisomers. Bp: 60–62 °C (5 mm). ¹⁹F NMR (188.24 MHz, CFC1₃): δ -77.9 (m, 3F), -67.8 (m, 2F), [-47.3 (t, J = 9.5 Hz), -48.0 (q, J = 9.5 Hz) (major set), -55.7 (t, J = 6.0 Hz), -56.0 (q, J = 6.0 Hz)] (2F total). Anal. Calcd for C₅Cl₂F₇O₂: C, 18.12; Cl, 32.09; F, 40.13. Found: C, 17.55; Cl, 32.30; F, 39.84.

IV. 2-(Chlorodifluoromethyl)-2-(trifluoromethyl)-4,5-difluoro-1,3-dioxole (CTD; 11). This monomer was prepared from the dechlorination of 2-(chlorodifluoromethyl)-2-(trifluoromethyl)-4,5-dichloro-4,5-difluoro-1,3-dioxolane with LiAlH₄/TiCl₄ reagents as described above. This monomer is a clear liquid. Bp: 58 °C. ¹⁹F NMR (188.24 MHz, CFC1₃): δ -82.0 (t, J = 12 Hz, 3F), -71.0 (q, J = 12 Hz, 2F), -161.4 (s, 2F). Anal. Calcd for C₅ClF₇O₂: C, 23.05; Cl, 13.61; F, 51.05. Found: C, 22.84; Cl, 13.71; F, 50.90.

Typical Procedures for Homopolymerization and TFE Copolymerization of Fluorodioxole Monomers. I. Homopolymerization. A 75-mL stainless steel shaker tube was cooled, evacuated, and charged with 1,1,2-trichloro-1,2,2-trifluoroethane (F-113; 20 g, 0.1067 mol), dioxole monomer (4 g, 0.0136 mol), and bis(4-tert-butylcyclohexyl) peroxydicarbonate initiator (0.10 g). This tube was cooled, evacuated, and agitated at 50–65 °C for

Table I. Homopolymers from Perfluorodioxole Monomers A

monomer	bp (°C)	X	R ₁	R ₂	T _g (°C)
1	33	F	CF ₃	CF ₃	330
2	16	F	F	CF ₃	212
3	0	F	F	F	180
4	40	F	C ₂ F ₅	F	150
5	42.5	F	C ₂ F ₅	CF ₃	118–139
6	52	F	C ₂ F ₅	C ₂ F ₅	a
11	58	F	CF ₂ Cl	CF ₃	330
12	44	H	CF ₃	CF ₃	256
13	42	CF ₃	CF ₃	CF ₃	a
15	55	Cl	CF ₃	CF ₃	a

^a No homopolymer formation from these monomers under the experimental conditions.

3 h under autogenous pressure. The polymer formed inside the tube was collected, dried in air, washed thoroughly with water, and then placed in a vacuum (150 mm) oven at 100 °C for 24–48 h to remove any volatile material. The white polymer obtained was submitted for DSC (differential scanning calorimetry) to determine the glass transition temperature (T_g), which is listed in Table I.

No homopolymerization was observed for monomers 6, 13, and 15.

II. Copolymerization with TFE. A stainless steel shaker tube was cooled, evacuated, and charged with 1,1,2-trichloro-1,2,2-trifluoroethane (F-113; 25 g, 0.133 mol), dioxole monomer (4 g, 0.0136 mol), bis(4-*tert*-butylcyclohexyl) peroxydicarbonate initiator (0.12 g), and TFE (1.0 g, 0.01 mol). This tube was then agitated for 2 h at 60 °C and 2 h at 70 °C under autogenous pressure. The polymer formed inside the tube was collected, dried in air, washed thoroughly with water, and then placed in a vacuum (150 mm) oven at 100 °C for 24–48 h to remove any volatile residue. The white polymer obtained (usually in 60–

90% conversion) was submitted for DSC to determine the glass transition temperature (T_g). The compositions of the copolymers were determined by ¹⁹F high-temperature melt NMR spectroscopy. The relationship of T_g vs copolymer composition is plotted in Figure 1.

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References and Notes

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