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Perfluoro-4-methyl-1,3-dioxole: a new monomer for high-T_g amorphous fluoropolymers

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Abstract

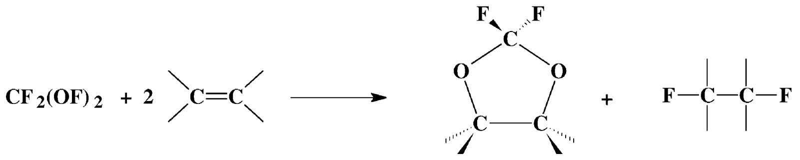
A 4-Chloro-5-trifluoromethyl-2,2,4-trifluoro-1,3-dioxolane (**1**) was synthesised by reaction of $CF_2(OF)_2$ with CF_3–CH=CFCl; the elimination of HCl from (**1**) in basic conditions led to the formation of dioxole perfluoro-4-methyl-1,3-dioxole (**2**). Both these synthetic steps gave the corresponding product in high yield.

A new synthetic route for the preparation of CF_3–CH=CFCl, starting from CF_2ClBr and $CH_2=CF_2$, together with some examples of polymerisation products obtained by reaction of dioxole (**2**) with fluoroolefins are also reported.

Keywords: Bis(fluoroxy)difluoromethane; Reactivity; Synthesis; Chlorofluoro propenes; Isomerization; Dioxolanes; Perfluorodioxoles

1. Introduction

The low temperature reaction of $CF_2(OF)_2$ with alkenes was found to lead to the formation of 2,2-difluoro-1,3-dioxolanes (Eq. (1)) [1,2], as well as to linear haloethers depending on the reaction conditions adopted [4]. These intermediates are useful for the preparation of sophisticated perfluoro monomers, which are building blocks for the industrial synthesis of amorphous perfluoropolymers having T_g*s* within the exceptionally wide range of +300 to −70 °C [3–7].

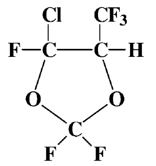


Eq.(1)

Perfluorodioxoles based polymers are similar to poly(tetrafluoroethylene) in their chemical and thermal stability, but they have enhanced physical and mechanical properties, better optical clarity, and lower dielectric constants. In addition, these polymers may be soluble in selected fluorinated solvents. These unique characteristics make fluorodioxole containing polymers good candidates for gas separation membranes, advanced electronic, optical, and biomedical applications. In the light of these considerations, new fluorodioxoles and new synthetic methods for their preparation have received particular attention.

In the literature, halogenated 2,2-difluoro-1,3-dioxolanes have been prepared using multistep processes often with low or inconsistent yields [5]. As an alternative, the chemistry of $CF_2(OF)_2$ provides a direct and versatile way to obtain dioxolane rings [2].

Herein, we report the synthesis of 4-chloro-5-trifluoromethyl-2,2,4-trifluoro-1,3-dioxolane (**1**) and perfluoro-4-methyl-1,3-dioxole (**2**) together with some examples of the polymeric materials obtained from dioxole (**2**) and fluoroolefins.



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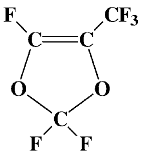

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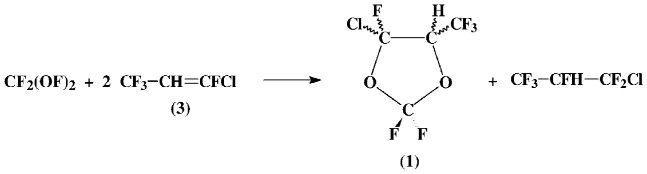
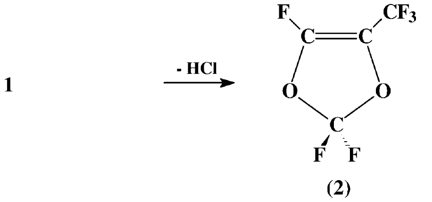
2. Results and discussion

Dioxolane **1** and dioxole **2** were prepared, in high yield, as shown below:



Eq.(2)



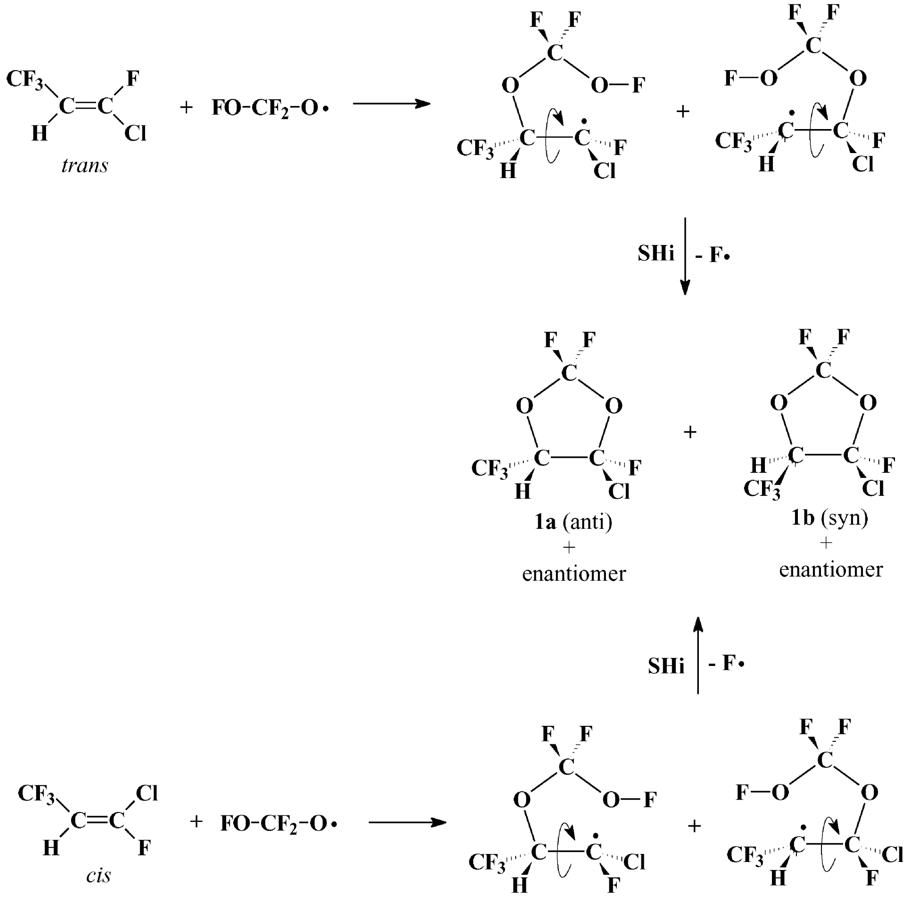
Eq.(3)

The first step of the synthesis (Eq. (2)) leads to the formation of the 4-chloro-5-trifluoromethyl-2,2,4-trifluoro-1,3-dioxolane **1** both in the *anti* isomer **1a** (in which the CF_3 group and the chlorine atom are in *anti* position) and in the *syn* isomer **1b** (in which the CF_3 group and the chlorine atom are in *syn* position) with an isomer ratio $anti/syn = 6/4$.

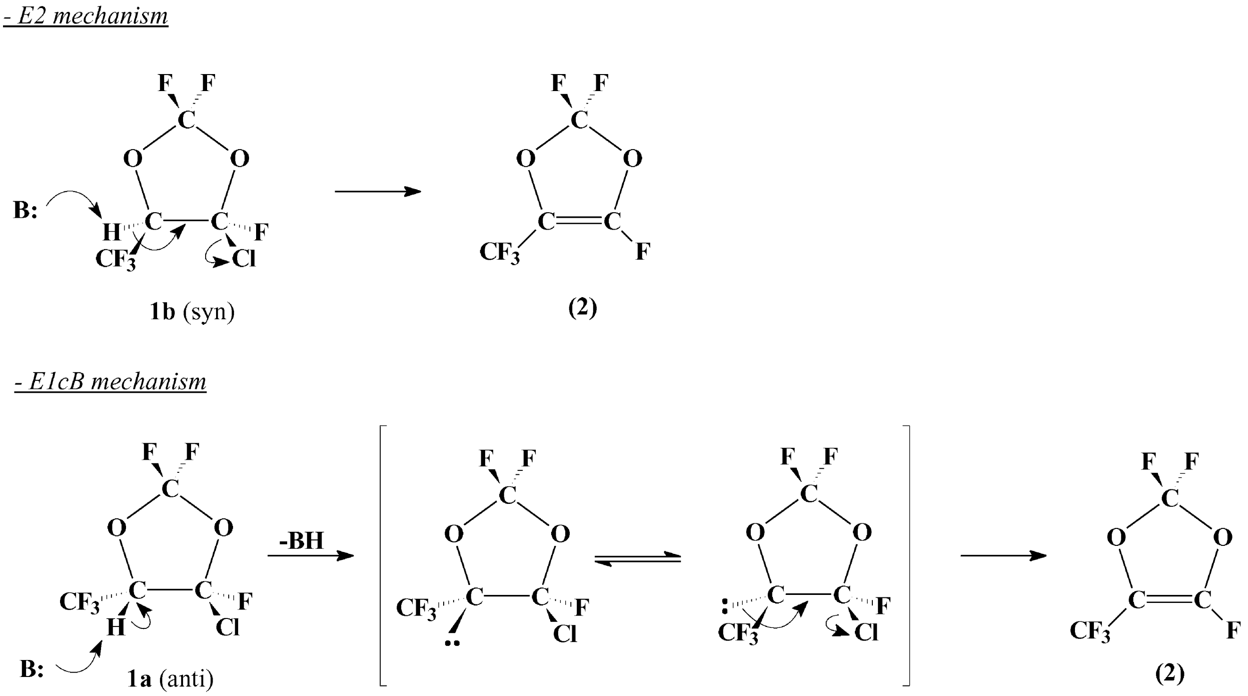
Since the starting olefin **3** had a *trans*/*cis* ratio equal to 6/4 this result indicates that the reaction which leads to the formation of the dioxolane ring, may be faster than the rotation of the radical intermediate (Scheme 1). This suggestion seems to be in contrast with an earlier finding that the *syn*/*anti* geometry of the dioxolane products is independent of the starting olefin [2]. This paradox may be explained by the higher rotation barrier energy of the radical intermediate in the present case due to the bulkier CF_3 group as compared with hydrogen and chlorine.

In fact, the *anti* configuration of the dioxolane ring should be preferred because of the steric hindrance between the CF_3 group and the chlorine atom, therefore the *syn* olefin should lead to the *anti* isomer as the major product, resulting in a larger amount of the *anti* isomer among the reaction products.

In order to prepare dioxoles from dioxolanes a general method of synthesis reported in the chemical literature consists of a dehalogenation reaction, usually dechlorination, of a dioxolane ring in which one chlorine atom is present at the 4-position and one at the 5-position of the ring. The dehalogenation reactions are usually carried out with a metal (Zn, Mg) in polar aprotic solvents (in particular DMF and DMSO). Such dehalogenation constitutes a problem in the perfluorodioxole synthesis, because it usually gives low yields.



Scheme 1.



Scheme 2.

Generally the dehalogenation yield increases if, in the starting dioxolane, the relative amount of the *anti* isomer (in which the two chlorine atoms are *anti*) is higher than that of the *syn* isomer (in which the two chlorine atoms are *syn*) [8].

In this work, the substituents at the 4- and 5-positions of the dioxolane have been properly chosen in order to obtain the dioxole **2** by a dehydrochlorination reaction (Eq. (3)) in place of the generally used dehalogenation reaction. This reaction was carried out with NaOH or KOH aqueous solutions under phase transfer conditions. Both the *anti* isomer **1a** and the *syn* isomer **1b** gave the dioxole product **2** in good yield. The mechanism that leads to the product could be different for the two isomers. It seems likely that an E_2 elimination should be favoured for the *syn* isomer **1b** in which the hydrogen atom and the chlorine atom are *anti* to one another, while for the *anti* isomer **1a** it seems more likely that the reaction proceeds through an E1cB mechanism (Scheme 2).

It should be noted that even if the dehydrohalogenation reaction could also lead to elimination of HF in place of HCl, in our experiments the reaction was totally selective toward the HCl elimination.

The starting olefin CF_3–CH=CFCl (**3**) was prepared by a three-step original approach (Eqs. (4)-(6)):

$$CF_2BrCl + CH_2{=}CF_2 \xrightarrow[120\,^{\circ}C]{(tBuO)_2} \underset{(4)}{CF_2Br{-}CH_2{-}CF_2Cl} \qquad Eq.(4)$$

$$4 \xrightarrow[PTC]{KOH} \underset{(5)}{CF_2{=}CH{-}CF_2Cl} \qquad Eq.(5)$$

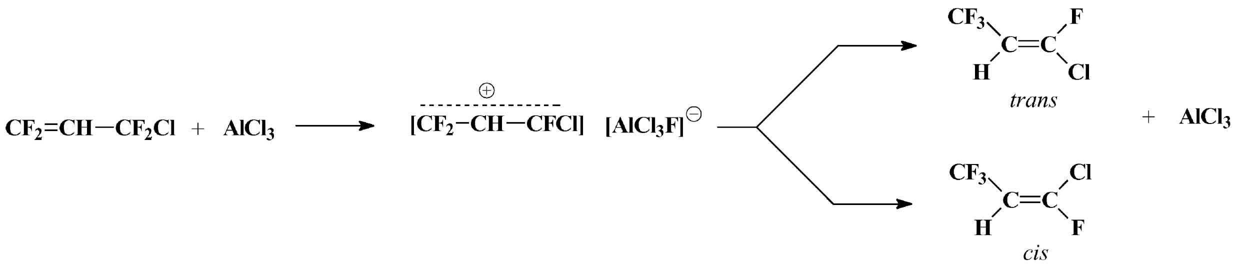
$$5 \xrightarrow{AlCl_3} \underset{(3)}{CF_3{-}CH{=}CFCl} \qquad Eq.(6)$$

A 1-Bromo-3-chloro-1,1,3,3-tetrafluoropropane (**4**) was prepared, in 62% yield, by a peroxide-initiated reaction of bromochlorodifluoromethane with vinylidene fluoride at 110 °C (Eq. (4)).

Dehydrohalogenation of **4** in phase transfer conditions gave, selectively, 3-chloro-1,1,3,3-tetrafluoropropene (**5**) in 84% yield. In this case also the dehydrohalogenation reaction could lead to elimination of HCl in place of HBr but it was totally selective toward HBr elimination suggesting an E2 type mechanism [9].

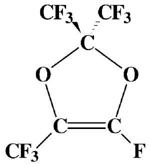
Compound **5** isomerised in 85% yield to a mixture (6:4) of *trans*- and *cis*-1-chloro-1,3,3,3-tetrafluoropropene (**3**) when treated with catalytic amount of $AlCl_3$ (Eq. (6)). The isomerization process likely involves an allylic cation as shown in Scheme 3.

As reported above, perfluorodioxoles are of interest as monomers in the preparation of fluoropolymers especially in the preparation of copolymers with tetrafluoroethylene (TFE). It has been reported by Hung that the steric bulkiness of the substituents in the 4- and 5-positions of the dioxole ring is critical for the polymerisation reaction rate [4]. Furthermore Hung reported that perfluoro-2,2,4-trimethyl-1,3-dioxole (**6**) failed to copolymerise with TFE. It seems that the low reactivity in the polymerisation reactions of **6** is due to the steric effect of the trifluoromethyl group at the 4-position. This conclusion may be reasonable if we consider that perfluoro-2,2-dimethyl-1,3-dioxole (**7**), in which the CF_3 group at 4-position in **6** is replaced by a fluorine



Scheme 3.

atom, is very reactive and it has also a tendency to homopolymerize even at a temperature as low as −78 °C.



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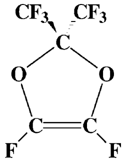
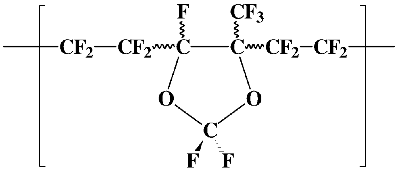


(7)

In contrast to dioxole **6**, the new dioxole **2** undergoes copolymerisation with TFE ($CF_2{=}CF_2$) and VDF ($CF_2{=}CH_2$) leading to the formation of novel copolymers comprising the new following units in the polymer chains [10].



(8)

This monomer failed to homopolymerize when initiated by perfluoropropionyl peroxide or AIBN in pure liquid dioxole. This tendency can also be seen in the copolymerization with TFE (*3.6.*) and VDF (*3.7*), where the dioxole incorporated in the polymer obtained is lower than 51% despite the high dioxole and low TFE or VDF concentrations [10].

In conclusion, two new compounds belonging to the family of 2,2-difluoro-1,3-dioxolanes and 1,2,3-trifluoro-4-perfluoroalkyl-1,3-dioxoles have been synthesised. An alternative synthesis of perfluoro-1,3-dioxoles from 1,3-dioxolanes has been reported in which a dehydrohalogenation reaction has been used in place of the generally used dehalogenation reaction. Although the olefin CF_3–CH=CFCl is a known compound [11], a new process for its synthesis is also reported.

Finally, the successful polymerisation reaction of **2** with TFE and VDF provides the possibility to obtain new fluorinated polymers, which may lead to valuable potential applications.

3. Experimental

General methods: Volatile compounds were handled in a glass and/or stainless-steel vacuum system equipped with glass/PTFE or stainless-steel valves. Pressures were measured with a Druck PDCR 110/W differential pressure gauge. Quantities of gaseous reactants and products were measured from measured volumes assuming ideal gas behaviour.

^{19}F NMR and ^{1}H NMR spectra were recorded on Varian 200 MHz and Varian 300 MHz instruments respectively with $CDCl_3$ as solvent and $CFCl_3$ or TMS as internal standards. GLC analyses were performed with a HRGC 5300 Carlo Erba instrument equipped with thermal conductivity detectors. Glc/ms spectra were performed on a Varian Mat CH7-A at 70 eV in the electron impact mode.

Materials: Chemicals were obtained from commercial sources and directly utilized.

Bis(fluoroxy)difluoromethane was prepared according to the standard methods described in the literature [12–15]. ***Caution!!* Appropriate precautions should be taken when handling hypofluorites [1]. Under certain conditions, these compounds are capable of an energetic explosive decomposition.**

3.1. *Preparation of 1-bromo-3-chloro-1,1,3,3-tetrafluoropropane (**4**)*

A 370 ml stainless steel reactor, equipped with a magnetic entrainment mechanical stirrer, was charged with CF_2BrCl (280 g, 1.7 mol) and *tert*-butyl peroxide (2.8 g, 0.02 mol). The reactor was then heated to 110 °C and fed for eight h with vinylidene fluoride (VDF) keeping the pressure inside the reactor between 15 and 20 atm. At the end of the reaction, 65 g (1.01 mol) of VDF had been fed. The reaction mixture was fractionally distilled to afford 145 g (0.63 mol) of **4** as a clear, colourless liquid. The yield of the reaction was 62%. Compound **4** has b.p. 85 °C.

$BrCF_2$–CH_2–CF_2Cl: ^{19}F NMR: $\delta_A = -41.9$ ppm (2F, tt); $\delta_B = -46.6$ ppm (2F, tt).

^{1}H NMR: 3.2 ppm (2H, tt). $J_{AB} = 12$ Hz; $J_{AH} = J_{BH} = 12$ Hz.

MS (EI) (*m/z*, [fragment]): 195 [M–Cl^+]; 149 [M–Br^+], 100%; 129 [CF_2Br^+]; 85 [CF_2Cl^+].

IR (cm^{-1}): 2980, 1364, 1218, 1182, 1148, 938, 800, 692, 642, 566.

Analysis: calc. for $C_3H_2F_4BrCl$: C, 15.69; F, 33.13%. Found: C, 16.08; F, 32.93%.

3.2. Preparation of 3-chloro-1,1,3,3-tetrafluoropropene (5)

Compound **4** (25 g, 0.11 mol) obtained as above was mixed with $(Bu)_4NOH$ (1.5 g) (40% (w/w) aqueous solution) in a reaction flask fitted with a dropping funnel, a magnetic stirrer, and a water-cooled condenser connected, via a trap cooled to −78 °C, to a vacuum system that was used to maintain a pressure of ca. 400 mm Hg.

The reaction mixture was heated to 45 °C and KOH aqueous solution (25 ml, 30% (w/w)) was added dropwise under vigorous stirring. At the end of the addition, the pressure was lowered to 200 mmHg and the reaction products, collected in the cold trap, were fractionally distilled to give the alkene **5** as a clear, colourless liquid, yield: 13.7 g (83%). Compound **5** has b.p. 14 °C.

$ClCF_2$–CH=CF_2: ^{19}F NMR: $\delta_A = -51.0$ ppm (2F, ddd); $\delta_B = -71.6$ (1F, ddt); $\delta_C = -78.5$ (1F, ddt). ^1H NMR: $\delta = 5.05$ (1H, dtd). $J_{AB} = 21$ Hz; $J_{AC} = 9$ Hz; $J_{AH} = 9$ Hz; $J_{BC} = 9$ Hz; $J_{BH} = 22$ Hz; $J_{CH} = 1.5$ Hz.

MS (EI) (*m/z*, [fragment]): 148 [M^+]; 129 [M-F^+]; 113 [M-Cl^+], 100%; 85 [CF_2Cl^+]; 63 [$C_2F_2H^+$].

IR (cm^{-1}): 3144, 3098, 1758, 1372, 1269, 1227, 1098, 1008, 935, 831, 792, 580.

Analysis: calc. for C_3HF_4Cl: C, 24.2; F, 51.2%. Found: C, 24.5; F, 50.0%.

3.3. Preparation of 1-chloro-1,3,3,3-tetrafluoropropene, (3)

$AlCl_3$ (1 g, 0.007 mol) was added under stirring to **5** at −30 °C, in a flask (50 ml) fitted with a nitrogen inlet and a water-cooled reflux condenser connected, via a trap cooled to −196 °C, to a vacuum system. The reaction mixture was allowed to warm slowly up to 13 °C while a slow stream of nitrogen was passed through the apparatus during this period. The flow of nitrogen was then interrupted and the reaction products pumped off through the cold trap at 400 mm Hg. The products collected in the cold trap were then fractionally distilled to give compound **3** as a mixture (6/4) by ^{19}F and ^1H NMR spectroscopy of *trans*- and *cis*-1-chloro-1,3,3,3-tetrafluoropropene (13.6 g, 0.092 mol). Yield = 84%. Compound **3** has b.p. 17 °C.

CF_3–CH=CFCl: *cis-isomer* ^{19}F NMR: $\delta_A = -59.1$ ppm (3F, dd); $\delta_B = -62$ ppm (1F, qd). ^1H NMR: 5.78 ppm (1H, qd). $J_{AB} = 14$ Hz; $J_{AH} = 6$ Hz; $J_{BH} = 8$ Hz.

trans-isomer: ^{19}F NMR: $\delta_A = -59.2$ ppm (3F, dd); $\delta_B = -60.7$ ppm (1F, qd). ^1H NMR: 5.38 ppm (1H, qd). $J_{AB} = 17$ Hz; $J_{AH} = 7$ Hz; $J_{BH} = 25$ Hz.

MS (EI) (*m/z*, [fragment]) (isomers mixture): 148 [M^+]; 129 [M-Cl^+], 100%; 69 [$CF3^+$].

IR (cm^{-1}) (isomers mixture): 3127, 1748 (*cis*), 1691 (*trans*), 1353, 1268, 1197, 1165, 1110, 1062, 859, 672.

Analysis: calc. for C_3HF_4Cl: C, 24.2; F, 51.2%. Found: C, 24.0; F, 50.6%.

3.4. Preparation of 4-chloro-5-triluoromethyl-2,2, 4-trifluoro-1,3-dioxolane (1)

In a 200 ml multi-necked cylindrical glass reactor equipped with mechanical stirrer, thermocouple, dipping inlet for the reaction gaseous mixture, outlet with inert gas flow, 51.3 g (0.346 mol) of **3** were introduced. The reactor was then brought by means of a cryostat to −70 °C and, under mechanical stirring, a mixture of $CF_2(OF)_2$ (1 l/h) and helium (3 l/h) was continuously fed for 1.9 h. The reaction products were separated by fractional distillation to give 28.9 g of **1** as a mixture (4/6 by ^{19}F and ^1H NMR spectroscopy) of *syn*- and *anti*-isomers, yield (based on $CF_2(OF)_2$): 72.8%. Compound **1** has b.p. 56 °C.

$CH(CF_3)$-CFCl-O-CF_2-O:: *syn*-isomer: ^{19}F NMR: $\delta_A = -75.8$ ppm (3F,); $\delta_B = -47.8$ ppm (1F,). ^1H NMR: 5.05 ppm (1H,).

anti-isomer: ^{19}F NMR: $\delta_A = -75$ ppm (3F, dd); $\delta_B = -68.3$ ppm (1F,). ^1H NMR: 5.12 ppm (1H,).

MS (EI) (*m/z*, [fragment]) (isomer mixture): 195 [M-Cl^+]; 167 [$C_3F_6HO^+$], 100%; 161 [M-CF_3^+]; 148 [$C_3F_5HO^+$]; 101 [$C_2F_4H^+$]; 69 [CF_3^+].

IR (cm^{-1}) (isomers mixture): 2998, 1383, 1307, 1279, 1194, 1116, 1078, 989, 921, 840, 707.

Analysis: calc. for $C_4HF_6O_2Cl$: C, 20.8; F, 49.5%. Found: C, 20.4; F, 49.3%.

3.5. Preparation of perfluoro-4-methyl-1,3-dioxole (2)

Compound **1** obtained as above (9 g, 0.039 mol) was mixed with 1.5 g of $(Bu)_4NOH$ (40% (w/w) aqueous solution) in a reaction flask (50 ml) fitted with a dropping funnel, a magnetic stirrer, and a water-cooled condenser connected, via a trap cooled to −196 °C, to a vacuum system that was used to maintain a pressure of ca. 400 mmHg. The reaction mixture was kept at room temperature while of KOH aqueous solution (25 ml, 30% (w/w)) was added drop wise under vigorous stirring. At the end of the addition of the KOH solution, the pressure was lowered to 60 mmHg and the reaction products, collected in the cold trap, were fractionally distilled to give 4.5 g (yield: 61.3%) of the dioxole **2** as a clear, colourless liquid and 2.19 g of the starting dioxolane **1**. The conversion of the reaction was 84.3% and the selectivity 72.7%. Compound **2** has b.p. 14–15 °C.

CF_3-C=CF-O-CF_2-O: ^{19}F-NMR: ^{19}F NMR: $\delta_A = -65.8$ (3F, d); $\delta_B = -130.4$ (1F, q); $\delta_C = -47$ (2F, s). $J_{AB} = 11$ Hz.

MS (EI) (*m/z*, [fragment]): 194 [M^+], 100%; 175 [M-F^+]; 147 [$C_3F_5O^+$]; 97 [C_2F_3O+]; 69 [CF_3^+].

IR (cm^{-1}): 1802, 1435, 1345, 1294, 1223, 1208, 1194, 1180, 1115, 1029, 992, 727, 491.

Analysis: calc. for $C_4F_6O_2$: C, 24.7; F, 58.8%. Found: C, 24.6; F, 58.1%.

3.6. Amorphous copolymer of perfluoro-4-methyl-1,3-dioxole with TFE

In a 50 ml steel reactor with magnetic stirrer and inlet for the reactant feeding and discharge, 1 ml of perfluoropropionyl peroxide at 6% by weight in CCl_2FCClF_2, 6.5 mmols of perfluoro-4-methyl-1,3-dioxole (PMD) and 10 mmol of uninhibited tetrafluoroethylene were introduced. The charged reactor was brought to −196 °C and evacuated, warmed to room temperature, cooled again to −196 °C and evacuated. The freezing and warming procedure was repeated twice; at the end of the degassing operations the reactor was brought to 30 °C and maintained at this temperature for 8 h under magnetic stirring. The reactor was then cooled to −196 °C, connected to a vacuum system at a pressure of 10^{-3} mbar, and allowed to reach room temperature while fractionating the vapours by traps cooled at −80, −120 and −196 °C. At the end of the fractionation, the trap at −80 °C contained CCl_2FCF_2Cl only, the trap at −120 °C contained 1.18 mmol of CCl_2FCF_2Cl and 6.1 mmol of unreacted dioxole and the trap at −196 °C contained 9.57 mmol of unreacted TFE. After solvent and unreacted monomers distillation and subsequent stripping of the polymer under vacuum at the temperature of 130 °C for 3 h, 40 mg of polymer were isolated. The mass balance of the unreacted monomers determined by g.l.c. indicated that the PMD percentage molar in the polymer was 48%. The polymer T_g, determined by DSC, was 165 °C; the DSC analysis did not show any residual crystallinity. The TGA showed a weight loss of 10% at 327 °C.

3.7. Amorphous copolymer of perfluoro-4-methyl-1,3-dioxole with VDF

In a 50 ml steel reactor with magnetic stirrer and inlet for the reactant feeding and discharge, 80 μl of perfluoropropionyl peroxide at 6% by weight in CCl_2FCClF_2 and 5 mmols of perfluoro-4-methyl-1,3-dioxole and 10 mmol of uninhibited VDF were introduced. The charged reactor was brought to −196 °C and evacuated, warmed to room temperature, cooled again to −196 °C and evacuated. The freezing and warming procedure was repeated twice; at the end of the degassing operations the reactor was brought to 30 °C and maintained at this temperature for 4 h under magnetic stirring. The reactor was then cooled to −196 °C, connected to a vacuum system at a pressure of 10^{-3} mbar, and allowed to reach room temperature while fractionating the vapours by traps cooled at −80, −120, and −196 °C. After solvent and unreacted monomers distillation and subsequent stripping of the polymer under vacuum at the temperature of 130 °C for 3 h, 175 mg of polymer were isolated. The mass balance of the unreacted monomers determined by g.l.c. indicated that the PMD percentage molar in the polymer was 50%. The polymer T_g, determined by DSC, was 60.9 °C; the DSC analysis did not show any residual crystallinity. The TGA showed a weight loss of 10% at 301 °C.

References

[1] W. Navarrini, V. Tortelli, A. Russo, S. Corti, J. Fluorine Chem. 95 (1999) 27–39.
[2] W. Navarrini, L. Bragante, S. Fontana, V. Tortelli, A. Zedda, J. Fluorine Chem. 71 (1995) 111–117.
[3] W. Navarrini, S. Corti, J. Fluorine Chem. Special issue: “Fluorine Chemistry in Italy” (Fit 290103b), in press.
[4] M.-H. Hung, Macromol. 26 (1993) 5829.
[5] E.N. Squire, US Patent 4,399,264 (1983).
[6] B.E. Smart, A.E. Feiring, C.G. Krespan, Z.Y. Yang, M.H. Hung, P.R. Resnik, Macromol. Symp. 98 (1995) 753–767.
[7] W. Navarrini, V. Tortelli, P. Colaianna, J.A. Abusleme, US Patent 5,646,223 (1997).
[8] W. Navarrini, S. Fontana, US Patent 5,296,617 (1994).
[9] J. March, Advanced Organic Chemistry, Wiley-Interscience Publication, New York, 1985, third ed., pp. 873–941.
[10] A. Russo, W. Navarrini, US Patent 6,469,185 (2002).
[11] J.H. Fried, W.T. Miller Jr, J. Am. Chem. Soc. 81 (1959) 2079.
[12] R.L. Cauble, G.H. Cady, J. Am. Chem. Soc. 89 (1967) 1962.
[13] F.A. Hohorst, J.M. Shreeve, J. Am. Chem. Soc. 89 (1967) 1809.
[14] P.G. Thompson, J. Am. Chem. Soc. 89 (1967) 1811.
[15] M.J. Fifolt, US Patent 4,499,024 (1985).