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Journal of Fluorine Chemistry 125 (2004) 189-197



www.elsevier.com/locate/jfluchem

New perfluorovinylethers through the bis(fluoroxy)difluoromethane (BDM) chemistry

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Received 29 January 2003; received in revised form 14 July 2003; accepted 28 July 2003

Abstract

In the present work we give an overview of the $CF_2(OF)_2$ radical reactivity and report the synthesis of new perfluorovinylethers. $CF_2=CF-OCF_2OCF_2CF_3$ and $CF_2=CF-OCF_2OCF_2CF_2OCF_3$ are prepared in a semi-continuous methodology starting from $CF_2(OF)_2$. These highly reactive vinylethers are characterized by the OCF_2O group directly bonded to the insaturation. For this reason they are excellent candidates for the preparation of very low T_g perfluororubbers.

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Keywords: Synthesis; Hypofluorites; Bis(fluoroxy)difluoromethane; Perfluorovinylethers; Perfluororubbers

1. Introduction

During the last decade the hypofluorite chemistry has attracted renewed interest from the industrial and academic world. The recently discovered reactivity of this class of compounds has in fact led to the identification of new interesting perfluoromonomers and polymers [1,2].

One of the most attractive issues of the hypofluorite chemistry is its great flexibility allowing the synthesis of diversified perfluorovinylether monomers [1,3–5]. These compounds represent the key building blocks for the preparation of different and innovative polymers, like amorphous fluoropolymers with T_g ranging from +300 °C [6,7] to -70 °C [2,15], as well as sulphonic and carboxylic perfluoropolymers for fuel cell applications [8].

Due to the unique properties of the O–F bond in the organic hypofluorite, this can act as a source of electrophilic fluorine [9], electrophilic alkoxylium species [10] as well as alkoxy radicals [11].

In our laboratories the chemistry of these compounds has been extensively studied. Their free-radical reactivity with fluoroolefins has been applied to the synthesis of perfluorovinylethers [12] as well as to the peculiar hypofluoriteinitiated oxygen copolymerization with perfluoroolefins [13].

One of the most versatile hypofluorite is the bis(fluoroxy)difluoromethane (BDM).

We have recently utilized this hypofluorite as intermediate for the preparation of sophisticated linear or cyclic vinylethers. These monomers are useful for the synthesis of high [6] or low T_g [2] amorphous fluoropolymers. In addition, a high content of vinylethers in the amorphous perfluoropolymer gives good solubility in perfluorinated solvents [14].

2. Results and discussion

The addition of BDM to the double bond, yields either the related dioxolane and the fluorinated olefin product, as described in Reaction 1, or the linear addition product, as shown in Reaction 2, depending on the reaction conditions adopted [5,7].

These two reactions evolve through similar initiation, propagation and termination steps as described in Scheme 1.



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^{0022-1139/\$ –} see front matter O 2003 Elsevier B.V. All rights reserved. doi:10.1016/j.jfluchem.2003.07.011



At the Propagation step 4 of Scheme 1, we have observed two competing propagation reactions. One is a monomolecular internal homolytic substitution S_{Hi} giving right of the dioxolane product, the second one is a bimolecular homolytic substitution S_{H} giving right of the linear addition product as shown in the reaction steps 4 and 4^b below:

4)
$$\begin{pmatrix} F,F \\ Q & F \\ C-C & F \\ C-C & S_{HI} \end{pmatrix} = \begin{pmatrix} F,F \\ F,F \\ Q & C \\ C-C \end{pmatrix} + F$$

4)^b $\begin{pmatrix} F_{i}F_{i}\\ C & -C \end{pmatrix}^{F} + FO \cdot CF_{2} \cdot OF \xrightarrow{K_{lim}} \begin{pmatrix} F_{i}F_{i}\\ F_{i} & -C \end{pmatrix}^{F} + FO \cdot CF_{2} \cdot O \cdot F + FO \cdot CF_{2} \cdot O \cdot F$

Initiation :

1) FO-CF₂·OF + C=C
$$\longrightarrow$$
 FO-CF₂·O· + F_{C-C} .

Propagation :



reaction media, whereas it is independent from the concentration of the radical intermediate FOCF₂OC-C• = [int.] as described in Eq. (1) where $K = K_{\text{lin}}/K_{\text{diox}}$:

$$\frac{\mathrm{lin}}{\mathrm{diox}} = \frac{K_{\mathrm{lin}}[\mathrm{CF}_2(\mathrm{OF})_2][\mathrm{int.}]}{K_{\mathrm{diox}}[\mathrm{int.}]} = K[\mathrm{CF}_2(\mathrm{OF})_2] \qquad \text{Eq. (1)}$$

In fact by increasing the BDM concentration in the reaction medium we observed an increment of the linear addition as compared to the cyclic addition depending also on the olefin, solvent and temperature chosen [5].

Under these experimental conditions, the olefin is added to the solution of BDM. This procedure is exactly the opposite of the methodology suggested in the literature in order to obtain high yield of hypofluorite addition products, where the addition order is reversed [11,12]. Hypofluorites are indeed susceptible to thermo or chemical self-decomposition that can cause very low addition yield or, in some cases, extended decomposition.

In particular, BDM has been found to be susceptible to ignition in gas or liquid phase, and this extended decomposition may be due to traces of organic or inorganic reactants. In order to safely handle BDM in gas phase a 1/3-dilution ratio with an inert gas like nitrogen or helium is needed [1]. In the liquid medium its behavior is more complex, since sudden exothermic reaction may locally and easily change both liquid and gas BDM concentration as well as the reaction course. This phenomenon has its experimental evidence as micro-explosion within the liquid phase. To avoid these hot spots, low temperature, low volume and high thermal exchange surface are needed.

The two pathways involve the same free-radical intermediate. Competition between cyclization to dioxolane and linear addition to bis-ethers has been observed. Considering the two reactions 4 and 4^{b} , it should be noted that ratio (lin/ diox) is proportional to the BDM concentration in the



D.D. DesMarteau and G.H. Cady suggested the use of very cold glass beads to be introduced in a millimoles scale batch reactor or the use of fluorinated solvents. Another approach is the use of a continuous system: the reactants are overcooled to -114 °C and spread in a film form on a cold vertical cylindrical reactor wall. In this way they can react at a temperature close to -110 °C, while reaching the outlet of the reactor, as described in Section 3.1. Following this latter procedure, the addition yields were good and the decomposition reactions were minimized even in the absence of solvent.

The BDM/TFE and BDM/CF₃OCF=CF₂ reactions are of particular interest since the linear intermediate hypofluorites (a) and (b) are utilized for the preparation of new perfluor-ovinylethers through their addition to CFCl=CFCl, as described in Schemes 2 and 3.

In the BDM/TFE reaction, to reduce the competitive dioxolane formation (Reaction 3 in Scheme 4), the ratio BDM/TFE should be at least 0.6. At higher ratio also the consecutive Reaction 2 can be minimized. In this way the yield to linear addition on converted BDM also increases, as can been seen by Fig. 1, where $linOF = CF_3CF_2OCF_2OF$ and $lin = CF_3CF_2OCF_2OCF_2CF_3$.

The experimental stationary points were obtained utilizing the apparatus and methodology described in Section 3.1. By changing the ratio between BDM/TFE of the reacting gases a set of stationary points was analyzed. The data were

1)
$$FOCF_2OF + CF_2 = CF_2 \xrightarrow{K_{iinOF}} CF_3CF_2OCF_2OF$$

2) $CF_3CF_2OCF_2OF + CF_2 = CF_2 \xrightarrow{K_{iin}} CF_3CF_2OCF_2OCF_2CF_3$
3) $FOCF_2OF + 2CF_2 = CF_2 \xrightarrow{CF_2 - CF_2} + CF_3CF_3$



CF,

directly obtained through the gas-chromatographic (GC) areas of the uncorrected GC peaks. In the BDM/TFE range ratio observed the dioxolane product evaluated by on-line GC and by end products distillation was below 1% and therefore considered constant in all the trials.

The experimental difficulty for the determination of the correction factors for $CF_3CF_2OCF_2OF$ was due to the preparation and handling of a pure sample. This intermediate was simply characterized through the ¹⁹F NMR analysis and through the relative addition product structure determination.

As can be see in Fig. 1 the yield on the converted BDM (selectivity) increases with the increasing ratio BDM/TFE. This set of experimental data can also be utilized to qualitatively determine the ratio between the observed kinetic constants K_{linOF} and K_{lin} of the consecutive reactions (1) and (2) of Scheme 4.

The reactions (1) and (2) follow a scheme of consecutive reactions with a order higher than one and can be described by the differential Eq. (2) [16]:

$$\frac{\partial [\text{linOF}]}{\partial [\text{BDM}]} = -1 + \frac{K_{\text{lin}}}{K_{\text{linOF}}} \frac{[\text{linOF}]}{[\text{BDM}]}$$
Eq. (2)

Applying this equation to a continuous reactor through the material balance of the inlet and outlet at the stationary







Fig. 1. Yield of CF₃CF₂OCF₂OF (linOF) and CF₃CF₂OCF₂OCF₂CF₃ (lin) on converted BDM.

points, we can substitute the differential with the relative discrete concentration difference between the inlet and the outlet at the stationary points. The concentrations can be substituted with the millimoles of the related products formed or reacted in the unit of time, since they are referred to the same reactor volume, thus obtaining the following equation:

$$\frac{K_{\rm lin}}{K_{\rm linOF}} = \frac{(\rm BDM)}{(\rm linOF)} \left[1 + \left(\frac{\Delta(\rm linOF)}{\Delta(\rm BDM)} \right) \right]$$
 Eq. (3)

Although the experimental values reported in Table 1 are obtained by applying Eq. (3) and through a semi-quantitative analysis, the average value of 0.41 for $K_{\text{lin}/K_{\text{linOF}}}$ indicates that, in the experimental condition studied, BDM is around 2.4 times more reactive than linOF. Therefore, a single OF in BDM is 1.2 times more reactive than OF in the LinOF, thus appearing very similar.

The addition products to CFCl=CFCl, CF₃CF₂OCF₂-OCFClCF₂Cl and CF₃OCF₂CF₂OCF₂OCF₂OCFClCF₂Cl, can be dehalogenated in good yields to the related perfluoroviny-lether monomers, as shown in Sections 3.3 and 3.4.

Table 1 BDM/TFE ratio values and the related $K_{\text{lin}}/K_{\text{linOF}}$ ratios in the range BDM/ TFE 0.7–1.6

BDM/TFE	$K_{ m lin}/K_{ m linOF}$	
0.70	0.34	
0.78	0.38	
0.87	0.40	
0.97	0.38	
1.08	0.47	
1.22	0.44	
1.59	0.45	

All the perfluorovinylethers obtained are characterized by the unit OCF₂O directly bonded to the insaturation of the vinyl monomer. These methylene-oxy-vinylether monomers (MOVE) homopolymerize and copolymerize with TFE or VDF. The polymerization reactions are carried out in solution and are initiated by the perfluoropropionyl peroxide that decomposes to carbon dioxide and perfluoroethyl radical that initiates the polymerization. The end-groups of the polymer thus obtained are completely perfluorinated and do not introduce polarity in the polymer, that may cause undesired aggregation and T_g misevaluations.

In this experimental conditions the only side reaction that can introduce polar groups, such as carbonyl fluoride, at the end of the polymer chains is a rearrangement of the growing carbon radical bearing an oxyalky group in α position. Low reaction temperature and a high reactivity of the comonomers can minimize carboxylic end-group formation as described by Ameduri et al. [15].

The polymerization reactions are summarized in Table 2.

In the homopolymers T_g 's evaluation, where the only reacting monomer is the vinylether, we experimentally

Table 2		
Polymerization	reactions	

	TFE (%)	FVE (%)	$T_{\rm g}$ (°C)
Section 3.5	_	100 (MOVE 1)	-35.4
Section 3.6	_	100 (MOVE 2)	-52.6
Section 3.7	76	24 (MOVE 1)	-21.4
Section 3.8	63	37 (MOVE 2)	-44.5
Section 3.9	77	23 (PVE)	+15
Section 3.10	77	23 (β-PDE)	-4.8

The values represent the molar monomer percentage contents incorporated in the polymers.

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observed slightly higher T_g 's than one would expect through a linearization plotting of the T_g with the weight percent of the vinylether monomer incorporated in the polymer. This is probably due to the higher content of carbonyl fluoride radicals located at the end of the homopolymer chains compared to the copolymer with TFE. It is worth observing that the Tg of the TFE copolymer with the MOVE 1 (CF₂=CFOCF₂OCF₂CF₃) monomer in Section 3.7 is lower as compared to the T_g of the copolymer obtained in the Section 3.9 with CF₂=CFOCF₂CF₃ (PVE), even at equal modifying vinylether molar quantity incorporated in the polymer. This is due to the higher O/C ratio in the MOVE 1 monomer than in the PVE monomer.

Surprisingly, the T_g of the copolymer of the TFE with CF₂=CFOCF₂CF₂OCF₃ (β -PDE) is higher than the one of the copolymer of the TFE with MOVE 1 (CF₂=CFOCF₂-OCF₂CF₃), since both copolymers have the same molar monomer content and the same O/C ratio. This can be probably explained by the position of the oxygen atom in the vinylether monomer side chain.

Indeed in the MOVE 1 monomer the unit OCF₂O is directly bonded to the insaturation, on the contrary in the β -PDE the unit OCF₂O is not present. In order to have a better understanding of the low T_g variation in amorphous TFE copolymers in relation to the oxygen atom position in the vinylethers side chain, it is useful to compare the T_g 's of the TFE/MOVE 2 (CF₂=CFOCF₂OCF₂CF₂OCF₃) copolymers with the copolymers TFE/CF₂=CFOCF₂CF₂OCF₂-OCF₃ at the same comonomer concentration, since also in this case both monomers have the same O/C ratio and only the MOVE 2 monomer contains the unit OF₂O directly bonded to the insaturation.

Some data regarding TFE/CF₂=CFOCF₂CF₂(OCF₂)_{*n*}-OCF₃ (n = 1-5) copolymers recently appeared in the patent literature [17] further indicating that the monomers having the unit OCF₂O directly bonded to the insaturation have a higher capability of decreasing the T_g 's of the TFE copolymers.

3. Experimental

¹⁹F NMR spectra were recorded on a Varian 200 MHz spectrometer with CFCl₃ as internal standard. GLC analyses were performed with a Carlo-Erba instrument equipped with thermoconductivity detectors. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR instruments. GLC/MS spectra were performed on a Varian Mat CH7-A at 70 eV in the electron impact mode. All boiling points are uncorrected.

Bis(fluoroxy)difluoromethane was prepared according to standards methods described in the literature [18].

Olefins and other chemicals were obtained from commercial sources and were purified appropriately as required.

Warning: Although it has been found that $CF_2(OF)_2$ has a good thermal stability, because fire and explosion can occur

on contact with organic reagents safety precautions must be taken in handling BDM [7].

3.1. General procedure, synthesis of CF₃CF₂OCF₂OCFClCF₂Cl perfluoro-1,2-dichloro-3, 5-dioxaheptane

A 300 ml cylindrical flow reactor with i.d. of 3 cm, was equipped with a magnetic dragging mechanical stirrer, a turbine with recycle of the reacting gas placed at 20 cm from the reactor top, an internal thermocouple, two internal copper pipes (0.25 in o.d.) for the reactants feeding, ending at about at 1 mm above the turbine, and a products outlet placed at the bottom of the reactor. The apparatus was kept vertically during the reaction.

In this reactor, inside of which the temperature was maintained at -114 °C, 1.1 l/h of CF₂(OF)₂ diluted with 3.3 l/h of He were fed through one of the two inlet pipes; a flow of 1.1 l/h of CF₂=CF₂ diluted with 0.7 l/h of He was introduced through the second inlet pipe. The feeding was continued for 6.6 h.

After the reactants contacted each other on the fast moving turbine (2000 rpm), an immediate and exothermic reaction took place, and the liquid reactants quickly moved on the perimetral wall and to the bottom of the reactor. The reaction products were extracted from the bottom of reactor through the product outlet (o.d. 0.25 in), by static dropping. The reactions products were then evaporated and continuously brought to room temperature, while the gaseous mixture flow (unreacted starting material, reaction product and the diluting helium) was monitored by gas-chromatography.

The reaction mixture flow, consisting of unreacted BDM, $CF_3CF_2OCF_2OF$, $CF_3CF_2OCF_2OF_2CF_3$ and the diluting He (TFE and the 1,3-perfluorodioxolane were completely absent) was continuously fed, under mechanical stirring, into a 250 ml reactor. This second reactor, maintained at the temperature of -70 °C, was equipped with a thermocouple, a dipping inlet for the incoming reaction mixture from the first reactor, an outlet with head of inert gas, and contained 72.6 g of dichlorodifluoroethylene.

At the end of the reagents addition (BDM, $CF_3CF_2OC-F_2OF$) into the second reactor, the reaction raw material was distilled by a 90 plates column at atmospheric pressure, collecting 41.5 g of the desired product (boiling point of 91 °C).

The yield of perfluoro-1,2-dichloro-3,5-dioxaheptene, calculated with the respect of the moles of $CF_2(OF)_2$ utilized, is 36%.

The remaining reaction products were mainly: CF₃CF₂-OCF₂OCF₂CF₃, CF₂ClCF₂Cl and 4,5-dicloroperfluoro-1,3-diossolano. The ¹⁹F NMR of these products is consistent with the ¹⁹F NMR known in the literature. Characterization of perfluoro-1,2-dichloro-3,5-dioxaheptene is reported below.

Boiling point at atmospheric pressure: 91 °C.

¹⁹F NMR δ: -51.1/-52.1 (AB sys, 2F, $-\text{OCF}_2\text{O}$ -, J = 78 Hz), -70.8/-71.4 (AB sys, 2F, C-CF₂Cl, J = 170 Hz), -77.4 (1F, m, OCFCl-), -87.6 (s, 3F, CF₃-C), -90.2/-90.8 (AB sys, 2F, C-CF₂-O, J = 158 Hz).

GC-MS m/z: 69 (CF₃⁺), 119 (C₂F₅⁺), 151/153 (C₂F₃Cl₂⁺), 185 (C₃F₇O⁺) 100%.

IR (cm⁻¹): 1407(w), 1235(vs), 1032(s), 929(w), 847(m).

3.2. Synthesis of $CF_3OCF_2CF_2OCF_2OCFClCF_2Cl$ perfluoro-1,2-dichloro-3,5,8-trioxanonane (isomer A) and $CF_3OCF(CF_3)OCF_2OCFClCF_2Cl$ perfluoro-1, 2-dichloro-3,5,7-trioxa-6-methyloctane (isomer B)

As in Section 3.1, 1.55 l/h of $CF_2(OF)_2$ and 4.5 l/h of He were fed through one of the two inlet pipes; through the second inlet pipe 1.4 l/h of CF_2 =CFOCF₃ perfluoromethylvinylether and 0.7 l/h of He were fed for about 4.5 h. The reaction mixture extracted from the bottom of the reactor was monitored by GC. The reaction mixture of the flowing gases, consisting mainly of unreacted BDM, CF₃OCF₂-CF₂OCF₂OF, CF₃OCF₂CF₂O-CF₂OCF₂OCF₃ and the diluting He (CF₂=CFOCF₃ was completely absent) was continuously fed into the second reactor containing 51 g of dichlorodifluoroethylene at the temperature of -70 °C.

At the end of the addition (4.5 h) the reaction mixture contained in the second reactor was distilled by a plate column at the reduced pressure of 250 mmHg, yielding 50 g of a mixture formed by two isomers, isomer A and isomer B, respectively, perfluoro-1,2-dichloro-3,5,8-trioxanonane and perfluoro-1,2-dichloro-3,5,7-trioxa-6-methyloctane in a 79:21 ratio. The mixture composition was determined by GC and ¹⁹F NMR. The isomers were separated by preparative GC.

The molar yield of isomer A + isomerB with respect to $CF_2(OF)_2$ was 38%. The remaining products were mainly: CF_2CICF_2CI , 4,5-dicloroperfluoro-1,3-dioxolane and CF_3 - $OCF_2CF_2OCF_2OCF_2CF_2OCF_3$. ¹⁹F NMR of these products are consistent with the ¹⁹F NMR known in the literature. The characterization of perfluoro-1,2-dichloro-3,5,8-trioxanonane (isomer A) and perfluoro-1,2-dichloro-3,5,7-trioxa-6-methyloctane (isomer B) is as follows.

Mixture boiling point (A 79%, B 21%) at 250 mmHg: 82 $^{\circ}\mathrm{C}.$

¹⁹F NMR δ. Isomer A: -50.9/-51.8 (AB sys, 2F,-OCF₂O-, J = 78), -70.6/-71.2 (AB sys, 2F, C-CF₂Cl, J = 170 Hz), -77.2 (m, 1F, OCFCl-C), -56.0 (t, 3F, CF₃O, J = 9 Hz), -90.0/-90.5 (AB sys, 2F, C-OC-CF₂OCO, J = 144 Hz), -90.8 (q, 2F, O-CF₂-COC, J = 9 Hz). Isomer B: -51.4 (AB sys, 2F -OCF₂O-), -70.8 (AB sys, 2F, C-CF₂Cl), -77.2 (m, 1F, OCFCl-C), -55.0 (dm, 3F, CF₃OC), -86.2 (m, 3F, OC(CF₃)CO), -100.1 (m, 1F, OCF(C)O).

GC–MS m/z. Isomer A: 69 (CF₃⁺), 119 (C₂F₅⁺) 100%, 151/153 (C₂F₃Cl₂⁺), 185 (C₃F₇O⁺), 251 (C₄F₉O₂⁺). Isomer B: 69 (CF₃⁺), 97 (C₂F₃O⁺), 135 (C₂F₅O⁺), 151/153 (C₂F₃Cl₂⁺), 185 (C₃F₇O⁺) 100%. IR(cm⁻¹) of the mixture A 79%, B 21%: 1388(w), 1288(vs), 1233(vs), 1151(w), 1104(vs), 1032(s), 846(m), 685(w).

3.3. Dehalogenation general procedure and synthesis of the CF₃CF₂OCF₂OCF=CF₂ perfluoro-3,5-dioxa-1-heptene "MOVE 1 monomer"

In a 250 ml three-necked flask, equipped with mechanical stirrer, thermometer, dropping funnel, distillation column equipped with water refrigerant and collecting trap maintained at -78 °C connected to a mechanical vacuum pump, 150 ml of DMF, 15 g of Zn dust, 0.5 g of K₂CO₃ and 100 mg of I₂ were introduced. The internal temperature was brought to 80 °C and 50 g of perfluoro-1,2-dichloro-3,5-dioxaheptane were added drop by drop. When the addition was over the mixture was allowed to react for about 50 min. At the end the internal pressure was gradually brought from 760 to 300 mmHg. After about 20 min the collecting trap, containing 34.2 g of perfluoro-3,5-dioxa-1-heptene (MOVE 1), was disconnected. The dehalogenation yield was 85%.

Characterization of perfluoro-3,5-dioxa-1-heptene.

Boiling point at atmospheric pressure: 42 °C.

¹⁹F NMR δ : -57.0 (m, 2F, -OCF₂O–), 87.9 (s, 3F, CF₃– C), -90.7 (t, 2F, C–CF₂–O, J = 11 Hz), -116.5 (dd, 1F, O– C=CF, J = 87 Hz, J = 67.5 Hz), -123.2 (ddt, 1F, OC=CF, J = 112 Hz, J = 87 Hz, J = 5 Hz), -138.0 (ddt, 1F, O– CF=C).

GC–MS m/z: 69 (CF₃⁺), 81 (C₂F₃⁺), 97(C₂F₃O⁺), 119 (C₂F₅⁺) 100%, 147 (C₃F₅O⁺), 185 (C₃F₇O⁺), 216 (C₄F₈O⁺), 282 M^+ .

IR (cm^{-1}) : 1839(m), 1407(w), 1307(vs), 1245(vs), 1117(vs), 907(m), 846(m).

3.4. Synthesis of the "MOVE 2 monomer" $CF_3OCF_2CF_2OCF_2OCF=CF_2$ perfluoro-3,5,8-trioxa-1-nonene (isomer A) and the MOVE $CF_3OCF(CF_3)OCF_2OCF=CF_2$ (isomer B) perfluoro-3,5,7-trioxa-6-methyl-1-octene

As in Section 3.3, 110 ml of DMF, 10 g of Zn dust and 0.3 ml of Br_2 were introduced in the 250 ml flask. The internal temperature was brought to 80 °C and 30.5 g of a binary mixture prepared in Section 3.2 (perfluoro-1,2-dichloro-3,5,8-trioxanonane (79%) and perfluoro-1,2-dichloro-3,5,7-trioxa –6-methyloctane (21%)) were added drop to drop. When the addition was over, the mixture was allowed to react for about 3 h. At the end the internal pressure was reduced to 200 mmHg, after about 30 min the collecting trap was disconnected. The corresponding content was washed with water and dried over sodium sulphate obtaining 24.0 g of a mixture consisting of isomer A and isomer B in a 79:21 ratio. The overall dehalogenation yield was 98%. The two isomers were separated by preparative gas chromatography.

Characterization of the MOVE perfluoro-3,5,8-trioxa-1nonene (isomer A) and the MOVE perfluoro-3,5,7-trioxa-6methyl-1-octene (isomer B).

Boiling point range of the isomer mixture at atmospheric pressure: 72.5–74.5 °C.

¹⁹F NMR δ . Isomer A: CF₃OCF₂CF₂OCF₂OCF=CF₂: -56.5 (t, 3F, CF₃O-, J = 9 Hz), -57.1 (m, 2F, -OCF₂O-), 90.8 (t, 2F, C-CF₂-O, J = 11 Hz), -91.2 (q, 2F, O-CF₂-C, J = 9 Hz), -116.5 (dd, 1F, O-C=CF, J = 87 Hz, J = 66.5 Hz), -123.2 (ddt, 1F, OC=CF, J = 87 Hz, J = 112 Hz), -138 (ddt, 1F, O-CF=C, J = 112 Hz, J = 66.5 Hz).

Isomer B: CF₃OCF(CF₃)OCF₂OCF=CF₂: -55.6 (dq, 3F, CF₃O–), -57.1 (m, 2F, $-OCF_2O$ –), 86.7 (m, 3F, CF₃–C), -100.3 (m, 1F, -CF–), -116.5 (dd,1F, O–C=CF, J = 87 Hz, J = 66.5 Hz), -123.2 (ddt, 1F, OC=CF, J = 112 Hz, J = 87 Hz), -138 (ddt, 1F, O–CF=C, J = 112 Hz, J = 66.5 Hz).

GC-MS m/z. Isomer A: 69 (CF₃⁺), 81 (C₂F₃⁺), 97 (C₂F₃O⁺), 119 (C₂F₅⁺) 100%, 147 (C₃F₅O⁺), 185 (C₃F₇O⁺), 251 (C₄F₉O₂⁺), 282 (C₅F₁₀O₂⁺), M^+ .

Isomer B: 69 (CF₃⁺), 81 (C₂F₃⁺), 97 (C₂F₃O⁺), 119 (C₂F₅⁺) 100%, 147 (C₃F₅O⁺), 185 (C₃F₇O⁺), 282 (C₅F₁₀O₂⁺), M^+ .

IR (cm⁻¹) of the AB mixture: 1839(m); 1343(s); 1248(vs); 1245(vs); 1145(vs); 918(m); 889(m).

3.5. Homopolymerization of "MOVE 1" monomer perfluoro-3,5-dioxa-1-heptene

In a glass reactor of the volume of 20 ml, equipped with PTFE stopcock and magnetic stirring, 20 µl of 3% (w/w) perfluoropropionyl peroxide solution in CF₂ClCFCl₂, and 3 g of the perfluoro-3,5-dioxa-1-heptene "MOVE 1" prepared in 3.3 were charged. The reactor was cooled to -196 °C, evacuated, warmed to room temperature, cooled again to -196 °C and evacuated. The freezing and thaw procedure was repeated twice. At the end of the degassing operation the reactor was thermostated at 30 °C while stirring for 2 days. The reactor was then cooled to -196 °C and a second portion of 20 µl of perfluoropropionyl peroxide solution was charged under dry nitrogen atmosphere. After three degassing operations as described above, the reactor was thermostated at 30 °C while stirring for 2 days. A third 20 µl portion of perfluoropropionyl peroxide was finally added following the standard procedure and the reactor was left under stirring at 30 °C for 2 days.

The reaction raw material appears as a viscous, transparent, colorless and homogeneous solution.

After distillation of the unreacted monomer, and subsequent stripping under vacuum at 150 °C for 3 h, 260 mg of the homopolymers were isolated.

The IR analysis of the obtained polymer showed the absence of the absorption bands corresponding to the fluorinated monomer insaturation. The ¹⁹F NMR carried out on the polymer dissolved in perfluorobenzene is in accordance with the homopolymer structure having a molecular weight of 50,000. This analysis showed the absence of unreacted monomer. The DSC graph did not show any melting endothermic curve, wherefore the polymer was amorphous. The polymer T_g , evaluated by DSC, is -35.4 °C. The TGA analysis showed a weight loss of 2% at 332 °C and of 10% at 383 °C.

3.6. Copolymer between "MOVE 2 monomers" perfluoro-3,5,8-trioxa-1-nonene (isomer A) and perfluoro-3,5,7-trioxa-6-methyl-1-octene (isomer B)

In a glass reactor of the volume of 20 ml, equipped with PTFE stopcock and magnetic stirring, the following components were charged: 3.2 g of a MOVE mixture prepared according to 3.4 consisting of perfluoro-3,5,8-trioxa-1nonene 83% and perfluoro-3,5,7-trioxa-6-methyl-1-octene 17%. Following the procedure described in Section 3.5, 150 µl of 3% (w/w) perfluoropropionyl peroxide solution in CF₂ClCFCl₂ were added in three separated 50 µl portion. After following the polymerization procedure, the reaction raw materials appear as a slightly viscous, transparent, colorless and homogeneous solution. After distillation of the unreacted monomer, and subsequent stripping under vacuum at 150 °C for 3 h, 380 mg of the homopolymers were isolated. The IR analysis of the obtained polymer showed the absence of the absorption bands corresponding to the fluorinated monomer insaturation.

The ¹⁹F NMR carried out on the polymer dissolved in perfluorobenzene is in accordance with the copolymer structure having a molecular weight of 35,000 and the incorporated monomer ratio equal to the ratio of the reacting MOVE monomers. This analysis showed the absence of unreacted monomer. The DSC graph did not show any melting endothermic curve, therefore the polymer was amorphous. The polymer $T_{\rm g}$, evaluated by DSC, is -52.6 °C. The TGA analysis showed a weight loss of 2% at 280 °C and of 10% at 327 °C.

3.7. Amorphous copolymer between "MOVE 1 monomer" perfluoro-3,5-dioxa-1-heptene and TFE (general TFE copolymerization procedure)

In a AISI-316 Parr microreactor of the volume of 40 ml, equipped with magnetic stirring, pressure transducer and an inlet for the reactant feeding and discharge, 250 μ l of 3% (w/w) perfluoropropionyl peroxide solution in CF₂ClCFCl₂, 9.8 mmol of perfluoro-3,5-dioxa-1-heptene "MOVE 1 monomer" and 18 mmol of tetrafluoroethylene were introduced. The reactor was then cooled to -196 °C, evacuated, warmed to -78 °C and cooled again to -196 °C and evacuated. This procedure was repeated twice.

At the end of the degassing operations the reactor was thermostated at 30 °C while stirring for about 8 h. The internal pressure decreased from 6.4 to 4.7 atm. The reaction

was quenched by cooling the reactor at -78 °C, while the unreacted monomers were distilled under vacuum. The copolymer was then stripped at 150 °C at 10^3 mmHg for 3 h, yielding 1100 mg of copolymer.

The molar percentage of TFE and perfluoro-3,5-dioxa-1-heptene incorporated in the copolymer, determined by 19 F NMR analysis of the polymer dissolved in C₆F₆ at 50 °C were respectively 76 and 24%.

The IR analysis of the obtained copolymer shows the absence of the absorption bands corresponding to the monomers insaturation and the presence of very small absorption bands in the region of the carboxyl signals. The intensity of these signals, compared with the analogous one obtained from a film normalized at the identical thickness obtained with a similar copolymer prepared in Section 3.9, is equal to about 1/10 of the latter.

The DSC graph did not show any melting endothermic curve, wherefore the polymer was amorphous. The polymer T_g , evaluated by DSC, is -21.4 °C. The TGA analysis showed a weight loss of 2% at 450 °C and of 10% at 477 °C. The polymer intrinsic viscosity measured at 30 °C in Fluorinert[®] FC-75, is 35.5 ml/g.

3.8. Amorphous copolymer between TFE and "MOVE 2 monomers": perfluoro-3,5,8-trioxa-1-nonene and perfluoro-3,5,7-trioxa-6-methyl-1-octene

In a polymerization reactor identical to that used in Section 3.7, 100 µl of 6% (w/w) perfluoropropionyl peroxide solution in CF2ClCFCl2, 9.7 mmol of "MOVE 2 monomers" mixture: perfluoro-3,5,8-trioxa-1-nonene (83%) and perfluoro-3,5,7-trioxa-6-methyl-1-octene (17%) prepared in 3.4 and 10 mmol of TFE were introduced in sequence. The general TFE copolymerization procedure described in Section 3.7 was then followed until the thermosetting at 30 °C. The internal pressure decreased from 3.6 to 2.7 atm in about 8 h. The reaction was quenched by cooling the reactor at -78 °C and the unreacted monomers were distilled under vacuum. The copolymer was then stripped at 150 °C at 10^{-3} mmHg for 3 h, yielding 652 mg of copolymer.

The molar percentage of TFE and MOVE 2 monomers incorporated in the copolymer, determined by ¹⁹F NMR analysis of the polymer dissolved in C_6F_6 at 50 °C were respectively 63 and 37%. The molar ratio of the MOVE monomers, perfluoro-3,5,8-trioxa-1-nonene/perfluoro-3,5,7-trioxa-6-methyl-1-octene incorporated in the polymer is 83/17 and it is equal to the starting MOVE 2 monomers feeding mixture.

The IR analysis of the obtained copolymer showed the absence of the absorption bands corresponding to the monomers insaturation.

The DSC graph did not show any melting endothermic curve, wherefore the polymer was amorphous. The polymer $T_{\rm g}$, evaluated by DSC, is -44.5 °C. The TGA analysis showed a weight loss of 10% at 451 °C. The polymer

intrinsic viscosity measured at $30 \degree C$ in Fluorinert[®] FC-75, is 16.7 ml/g.

3.9. Amorphous copolymer between TFE and perfluoropro-3-oxa-1-hexene (PVE)

In a polymerization reactor identical to that used in the previous examples, 250 μ l of 3% (w/w) perfluoropropionyl peroxide solution in CF₂ClCFCl₂, 9.7 mmol of PVE perfluoropro-3-oxa-1-hexene and 18 mmol of TFE were in sequence introduced.

The procedure described in Section 3.7 was followed until thermosetting at 30 $^{\circ}$ C while stirring for 8 h.

The reaction was quenched by cooling the reactor at -78 °C and the unreacted monomers were distilled under vacuum. The copolymer was then stripped at 150 °C at 10^{-3} mmHg for 3 h and 540 mg of copolymer were recovered.

The molar percentage of TFE and PVE perfluoropro-3oxa-1-hexene incorporated in the copolymer, determined by ¹⁹F NMR analysis of the polymer dissolved in C₆F₆ at 50 °C were respectively 77 and 23%.

The IR analysis of the obtained copolymer showed the absence of the absorption bands corresponding to the monomers insaturation and showed the presence of small absorption bands in the region of the carboxyl signals. The intensity of these signals, compared with the analogous signals obtained from a film normalized to the identical thickness, obtained with a similar copolymer prepared in Section 3.7, is 10 times higher.

The DSC graph did not show any melting endothermic curve, wherefore the polymer was amorphous. The polymer T_g , evaluated by DSC, is 15 °C. The TGA analysis showed a weight loss of 2% at 427 °C and of 10% at 463 °C. The polymer intrinsic viscosity measured at 30 °C in Fluorinert[®] FC-75, is 51 ml/g.

3.10. Amorphous copolymer between TFE and perfluoropro-3,6-dioxa-1-heptene $CF_3OCF_2CF_2OCF=CF_2$ (β -PDE)

In a polymerization reactor identical to that used in the previous examples, 250 μ l of 3% (w/w) perfluoropropionyl peroxide solution in CF₂ClCFCl₂, 10 mmol of perfluoropro-3,5-dioxa-1-heptene and 18 mmol of TFE were in sequence introduced.

The procedure already followed in Section 3.7 was adopted until thermosetting at 30 $^{\circ}$ C under stirring.

The molar percentage of TFE and perfluoro-3,6-dioxa-1-heptene incorporated in the copolymer, determined by 19 F NMR analysis of the polymer dissolved in C₆F₆ at 50 °C were respectively 77 and 23%.

The IR analysis of the obtained copolymer showed the absence of the absorption bands corresponding to the monomers insaturation. The DSC graph did not show any melting endothermic curve, therefore the polymer was amorphous. The polymer $T_{\rm g}$, evaluated by DSC, is -4.8 °C.

4. Conclusion

The present work describes the preparation and characterization of new perfluorovinylether monomers readily available from standard reactants in fluorine chemistry. This monomer family is characterized by a OCF₂O unit directly bonded to the insaturation. This structure gives to these monomers a high capability of decreasing the T_g 's of TFE and VDF copolymers. These intrinsic characteristics, straight synthesis and high T_g decreasing capability, make this monomer family a perfect candidate for the preparation of low T_g perfluororubbers.

Acknowledgements

We wish to thank Prof. Darryl D. DesMarteau and Prof. D. Sianesi for their suggestions and helpful discussions.

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