

MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Synthesis and Tribological Properties
of New Fluoro-Containing Oligomers

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Abstract—Oligomers based on (polyfluoroalkyl)methyl oxiranes and thiiranes was first synthesized by the cationic polymerization in the presence of boron trifluoride etherate. Molecular weights of the products were defined by cryoscopic method. It was found that synthesized oligomers can be used as additives to industrial lubricants and sulfur oligomers are of the greatest positive tribological effect.

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Perfluoropolyesters (PFPE) are the most popular organofluoric liquid polymers, which are widely used in industrial processes. Polymeric molecules PFPE of known foreign grade Krytox, Fomblin, and Demnum depending on the operating conditions can contain different end groups. Thus, for example, Fomblin Z03 includes OCF₃, Fomblin Z-DOL and Demnum SA, CH₂OH-groups, Fomblin Z-DIAC, carboxyl group [1]. Molecular weights of PFPE are also varied by manufacturers in accordance with the requirements of consumers. For example, for Fomblin Z-DOL they are in the range of 2000–8000 g mol⁻¹ [2].

Oil and lubricants are basic materials produced based on PFPE. However, the use of PFPE is limited, since it is known that under conditions of friction under high temperature (about 300°C) they disproportionate with a release of fluorides [3, 4]. Therewith a part of released highly reactive products is spent on the formation of metal salts on the friction surfaces that inhibits the formation of metal oxides [5] and improves the process of friction due to a monomolecular layer of salt, which is strongly bound to the surface of the pure metal [6]. The residue of fluorides was subjected to further oxidation that is the cause of the deterioration of anti-friction characteristics

of the used PFPE. In this case the oxygen atom in PFPE chain plays a role of an active element required for improving anti-friction characteristics of the lubricant due to metal salt formed on the its surface as a result of tribochemical reactions. Such active elements also include atoms of phosphorus, nitrogen, and sulfur [7, 8].

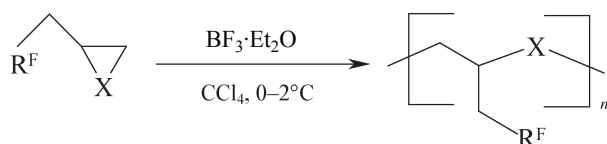
Using PFPE as an independent lubricating material is effective and contributes to the high resource conservation. There are many industrial fields, where oil and lubricant of the hydrocarbon nature are required, and PFPE could become effective additives to oils to increase viscosity and anti-friction characteristics. However, use of PFPE as additives to mineral oil is not possible, as they possess highly oleophobic nature and do not mix with the hydrocarbon fluids. Consequently, in the case of the use of fluorinated compounds as additives to mineral oils structures are required containing an oleophilic hydrocarbon moiety.

The aim of the study is the synthesis of oligomers based on polyfluorinated oxy- and thiiranes and examination of tribological properties of the resulting products.

The polymerization processes of oxirane and thiiranes of hydrocarbon nature were adequately studied in [9,

10]. Reactions of the formation of high molecular compounds from polyfluorinated oxiranes and thiiranes were insufficiently investigated.

For carrying out the polymerization by known procedures monomeric products were synthesized: oxiranes (**1a**) [11], (**1c**) [12] and thiiranes (**1b**, **1e**) [9], (**1d**) [13]:



X = O, R^F = C₄F₉ (**1a**), (**2a**), C₄F₉CH₂CHICH₂O (**1c**), (**2c**); X = S, R^F = C₄F₉ (**1b**), (**2b**), C₄F₉CH₂CHICH₂O (**1d**), (**2d**), H(CF₂)₂CH₂O (**1e**), (**2e**).

Previously it was shown that oxiranes containing fluoroalkyl substituents in initiating AlEt₃ as a result of cationic polymerization form high molecular weight products in the form of a viscous oil [14, 15]. However, use of AlEt₃ for polymerization requires special equipment. In this regard in the study boron trifluoride etherate (BF₃·Et₂O) was used as an initiator of the polymerization. This reagent previously well established itself in polymerization of non-fluorinated oxiranes [9] as well as in the synthesis of high molecular weight products from oxiranes similar by structure to compound **1c** [16].

The synthesized products **2a–2e** are novel and not described in literature. Previously it was found that the molecular weight M_w of the product analogous to compound **2a** with tridecafluoroalkyl substituent does not exceed 8000 g mol⁻¹ [16]. Determination of M_w was performed by static light scattering measurements in the solutions of the synthesized product in toluene according to Debye method using an instrument 90 Plus (Brookhaven Instrument Corporation, USA). Values of M_w allowed referring it to the low molecular weight polymers [16]. However, this technique is traditionally used to determine M_w , which is more than 10⁴ g mol⁻¹. This is due to the assumption that the macromolecule of large length is in the form of a coil conformation. Typically, the classical methods based on the phenomena ebullio and cryoscopy are used for lower molecular weight products.

In this connection, for determining M_w of products **2a–2e** the cryoscopic method was applied based on the

measurement of temperature lowering ΔT of freezing temperature of the solution of the test substance compared to pure solvent, which is related to M_w of the solute by the following equation [17]

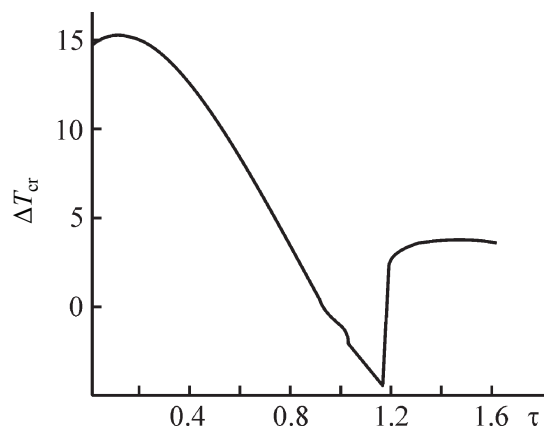
$$\Delta T = K \frac{10c}{M_w},$$

where c is the solution concentration (%), K , cryoscopic constant of the solvent.

Hexafluorobenzene was used as the solvent, CCl₄, as the calibration solution in hexafluorobenzene of a concentration of 3.04%. A typical thermogram of freezing for solution CCl₄ in hexafluorobenzene is shown in the figure. Thermogram clearly shows a gradual decline in the cell temperature at it cooling, the rapid rise in temperature at turning on a vibrator, and constant temperature of the cell contents in the crystallization process.

The measured values of freezing temperature of the pure solvent, hexafluorobenzene T_{cr} , the system CCl₄–hexafluorobenzene ΔT_{cr} and calculated values of K are listed in Table 1.

For measuring M_w solutions of compounds **2a–2d** were prepared in hexafluorobenzene at 25°C. Products **2a–2d** are highly soluble and in hexafluorobenzene they form homogeneous solutions. Mixing the compound **2e** with hexafluorobenzene results in heterogeneous emulsion, which was not suitable for measurements, so M_w of product **2e** was not determined. Table 2 shows the results of experimental measurements of ΔT_{cr} for



Thermogram of freezing the system CCl₄–hexafluorobenzene.. Concentration of CCl₄ 3.04%. (ΔT_{cr}) freezing temperature (°C), (τ) time (h).

Table 1. Results of determination of cryoscopic constant hexafluorobenzene

System	<i>c</i> , %	<i>T</i> _{cr}	Average value of <i>T</i> _{cr}	ΔT_{cr}	<i>K</i>
		°C			
Hexafluorobenzene	–	6.68 6.69 6.69 6.68	6.69	–	–
CCl ₄ in hexafluorobenzene	3.04	3.86 3.81 3.80 3.86	3.83	2.86	14.5

Table 2. Data for determining the molecular weight of compounds **2a–2d**

Compound	<i>c</i> , %	<i>T</i> _{cr}	ΔT_{cr}	<i>M</i> _w , g mol ⁻¹	<i>n</i>
		°C			
2a	9.90	5.45	1.23	1170	4.2
2b	6.98	6.18	0.51	2020	6.9
2c	9.99	5.75	0.93	1560	3.4
2d	8.57	6.14	0.54	2300	4.8

Table 3. Data on welding load and diameter of wear scar according to GOST 9490–75 of oligomer solutions **2b–2e** in industrial oil I-20A

Compound	Composition of the solution, wt % (I-20A : compound)	Welding load, H	Diameter of wear scar, ^a mm
I-20A	100.0 : 0.0	1120	0.7607
2b	99.5 : 0.5	1260	0.7117
2c	99.0 : 1.0	1410	0.5460
2c	98.0 : 2.0	1500	0.5133
2d	99.0 : 1.0	1600	0.4317
2d	98.0 : 2.0	1680	0.4387
2e	99.0 : 1.0	1330	0.5903

^a According to the results of four parallel measurements.

solutions of compounds **2a–2d**, the calculated values of *M*_w and effective polymerization degree *n*.

Analysis of the data of Table 2 demonstrates that the synthesized compound **2a–2d** are not polymeric but oligomeric products. Note that the oligomers **2b**, **2d** derived from thiiranes **1b**, **1d** are characterized by a

higher *M*_w than products **2a**, **2c** synthesized from oxiranes **1a**, **1c**. Presumably, this fact is associated with the known data of a higher reactivity of thiiranes compared to oxiranes [10].

Previously it was shown that a polymer with the tridecafluoroalkyl substituent similar in structure to

oligomer **2c** used as an additive to an industrial oil I-20A in the amount of 4 wt% improved the friction coefficient of the base oil in 2–3 fold [16]. Tests were carried out with the reciprocating movement of a plate–finger friction pair made of steel St. 18Cr9.

Oligomers **2a–2e** are of a limited solubility in the hydrocarbon oils (no more than 2 wt %). Under the conditions of ultrasonic dispersion several solutions of oligomers **2b–2e** were prepared in the oil-20A, which were stable for a long time (more than 1 month), and also their testing was conducted in accordance with State Standard (GOST 9490-75) “Methods for determination of tribological characteristics in four ball machine” and a weld load and a wear scar diameter were defined. The test results are listed in Table 3.

Analysis of the data of Table 3 shows that the results of all the tests are positive. Oligomer **2d** is of the greatest effect of improving the tribological characteristics of the oil I-20A and oligomer **2e**, of the lowest. Both oligomers belong to sulfur-containing compounds. Possible mechanism of further improving the tribological parameters of lubricant in the presence of sulfur-containing oligomers compared to the oxygen-containing is based on the formation of metal salts on the friction surface (sulfides, sulphates, etc.), as it was shown in studies [7, 8] and proved by X-ray photoelectron spectroscopy (XPS).

Lubricating the rubbing surfaces is affected by the length and nature of the fluoroalkyl substituent. The positive effect is smallest in the case of oligomer **2e**, whose short fluorinated substituent contains a terminal hydrogen atom that contributes to their poor operational parameters.

EXPERIMENTAL

Elemental analyzes were performed by an automatic analyzer Perkin–Elmer CHN PE 2400. IR spectra were recorded on a spectrophotometer Perkin–Elmer Spectrum One, NMR spectra, on a spectrometer Bruker DRX-400 (^1H : 400 MHz, relative to Me_4Si ; ^{19}F : 376 MHz, relative to C_6F_6).

Molecular weights were determined by a cryoscopic osmometer Knauer K7400 with software EuroOsmo 1.5. The sample of solution (or pure solvent) of 0.3–0.5 mL was placed in a glass vial, which was mounted in the unit

cell, cooled by the Peltier effect. A cell temperature -14°C providing hypothermia of the test solution was preset by the instrument software. The cell placed in a vial started cooling, therewith the sensor placed in it monitored the temperature of the test solution. At a certain temperature, which was -4°C in the measurements, the vibrator was turned on initiating rapid freezing of the vial. As a result, the temperature of the content quickly rose to the equilibrium freezing point, which remained constant until complete crystallization of the fluid. Measured freezing temperature was fixed by the sensor. Measurements were carried out sequentially for the pure solvent and solutions.

Synthesis of oxiranes **1a**, **1b** was carried out according to the procedures of [11, 12], respectively, their physicochemical characteristics coincide with the literature data. Synthesis of thiiranes **1b**, **1e** was carried out by the technique of [9], thiirane **1d**, by a research procedure in [13]. Synthesis of oligomers **2a–2e** was performed according to the study [16].

2-(2,2,3,3,4,4,5,5,5-Nonafluoropentyl) thiirane (1b). Colorless liquid, yield 64%, bp $142\text{--}147^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 3002 (C–H), 1223 (C–F). ^1H NMR spectrum (CDCl_3), δ , ppm: 2.25 m (2H, CF_2CH_2), 2.62 m [2H, $\text{CH}(\text{S})\text{CH}_2$], 3.02 m [1H, $\text{CH}(\text{S})\text{CH}_2$]. ^{19}F NMR spectrum (CDCl_3), δ , ppm (J , Hz): 35.84 m (2F, $\gamma\text{-CF}_2$), 37.59 m (2F, $\beta\text{-CF}_2$), 48.61 m (2F, $\alpha\text{-CF}_2$), 80.78 t.t (3F, CF_3 , $J_{\text{F,F}}$ 9.6, $J_{\text{F,H}}$ 3.2). Found (%): C 28.61, H 1.68, F 58.64, S 11.03. $\text{C}_7\text{F}_9\text{H}_5\text{S}$. Calculated (%): C 28.78, H 1.72, F 58.52, S 10.97.

2-[(4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyloxy) methyl]thiirane (1d). Yellow liquid, yield 83%, bp $112\text{--}114^\circ\text{C}/5$ torr. IR spectrum, ν , cm^{-1} : 2991, 2905, 2867 (C–H); 1217, 1167, 1130 (C–O–C, C–F). ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 2.20 m [1H, $\text{CH}(\text{S})\text{CH}_2$], 2.54 d [1H, $\text{CH}(\text{S})\text{CH}_2$, $J_{\text{H,H}}$ 6.2], 2.70 m (1H, CF_2CH_2), 3.09 m [2H, CF_2CH_2 , $\text{CH}(\text{S})\text{CH}_2$], 3.60 m [1H, CH_2OCH_2], 3.76 m (3H, CH_2OCH_2), 4.36 m (1H, CHI). ^{19}F NMR spectrum (CDCl_3), δ , ppm (J , Hz): 35.88 m (2F, $\gamma\text{-CF}_2$), 37.25 m (2F, $\beta\text{-CF}_2$), 47.91 m (2F, $\alpha\text{-CF}_2$), 80.76 t.t (3F, CF_3 , $J_{\text{F,F}}$ 9.6, $J_{\text{F,H}}$ 3.1). Found (%): C 25.01, H 2.03, F 35.73, S 6.54. $\text{C}_{10}\text{H}_{10}\text{F}_9\text{IOS}$. Calculated (%): C 25.23, H 2.12, F 35.91, S 6.73.

2,2,3,3-Tetrafluoropropylmethyl thiirane (1e). Colorless liquid, yield 75%, bp $80\text{--}82^\circ\text{C}/5$ torr. IR spectrum, ν , cm^{-1} : 2998, 2927 (C–H), 1108 (C–F). ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 2.21 m [1H

CH(S)CHH], 2.53 m [1H CH(S)CHH], 3.06 m [1H, CH(S)CH₂], 3.68 d [2H, OCH₂CH(S)CH₂, $J_{H,H}$ 6.2], 3.90 m (2H, CF₂CH₂OCH₂), 5.94 t.t (1H, HCF₂, $J_{H,F}$ 53.2, $J_{H,F}$ 5.0). ¹⁹F NMR spectrum (CDCl₃), δ, ppm: 22.06 d.m (2F, HCF₂, $J_{H,F}$ 53.2), 36.65 m (2F, CF₂CH₂). Found (%): C 34.83, H 3.79, F 36.27, S 14.47. C₇F₉H₅S. Calculated (%): C 35.30, H 3.95, F 37.22, S 15.70.

Typical procedure for the synthesis of oligomers 2a–2e. To a two-neck flask equipped with a reflux condenser, magnetic stirrer, and dropping funnel 50 mL of CCl₄ and 0.03 mole of oxirane **1a**, **1c**, or thiirane **1b**, **1c**, **1d** were added. Then, at 0–2°C 6 × 10⁻⁴ mol of BF₃·Et₂O was added. The reaction mixture was stirred for 1.5 hours at 0–2°C and 1.5 h at T_{room} 100 mL of water was added. The organic layer was washed with 2 M H₂SO₄, then with aqueous K₂CO₃, dried with MgSO₄, the solvent was distilled off, the residue was evacuated, and oligomers **2a–2e** were obtained.

Poly{oxy[1-(2,2,3,3,4,4,5,5,5-nonafluoropentyl) ethylene]} (2a). A viscous oil of light-yellow color, yield 54%, $M_w = 1170$ g mol⁻¹. IR spectrum, ν , cm⁻¹: 2939, 2882 (C–H); 1223, 1134 (C–O–C, C–F). ¹H NMR spectrum [(CD₃)₂CO], δ, ppm: 2.19–2.71 m (2H, CH₂CF₂), 3.48–4.32 m (3H, CH₂CHO). ¹⁹F NMR spectrum [(CD₃)₂CO], δ, ppm: 37.67–38.20 m (2F, γ -CF₂), 39.05–39.88 m (2F, β -CF₂), 49.05–52.82 m (2F, α -CF₂), 82.23–82.73 m (3F, CF₃). Found (%): C 29.85, H 1.74, F 61.97.

Poly{sulfanediyl[1-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)ethylene]} (2b). A viscous oil of light-brown color, yield 77%, $M_w = 2020$ g mol⁻¹. IR spectrum, ν , cm⁻¹: 2993, 2933 (C–H); 1222, 1171, 1134 (C–F). ¹H NMR spectrum (CDCl₃), δ, ppm: 2.23–2.81 m (2H, CF₂CH₂), 2.87–3.14 m (2H, CH₂CHS), 3.21–3.50 m (1H, CH₂CHS). ¹⁹F NMR spectrum (CDCl₃), δ, ppm: 35.23–36.12 m (2F, γ -CF₂), 36.90–37.43 m (2F, β -CF₂), 48.21–49.06 m (2F, α -CF₂), 80.00–80.96 m (3F, CF₃). Found (%): C 28.71, H 1.58, F 58.97, S 10.52.

Poly{oxy[1-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyl)ethylene]} (2c). A viscous oil of brown color, yield 59%, $M_w = 1560$ g mol⁻¹. IR spectrum, ν , cm⁻¹: 3059, 3000, 2873, 2347, 2181 (C–H); 1232, 1134 (C–O–C, C–F). ¹H NMR spectrum (CDCl₃), δ, ppm: 2.59–3.11 m (2H, CF₂CH₂), 3.43–3.88 m (7H, CH₂OCH₂, CH₂CHO), 4.31–4.41 m (1H, CHI). ¹⁹F NMR spectrum (CDCl₃), δ, ppm: 35.59–36.04 m (2F, γ -CF₂), 37.08–37.53 m (2F, β -CF₂), 46.83–49.29 m (2F, α -CF₂),

80.46–80.89 m (3F, CF₃). Found (%): C 26.11, H 2.19, F 37.32.

Poly{sulfanediyl[1-(4,4,5,5,6,6,7,7,7-nonafluoro-2-iodoheptyloxy)methyl]ethylene]} (2d). A viscous oil of dark-brown color, yield 77%, $M_w = 2300$ g mol⁻¹. IR spectrum, ν , cm⁻¹: 2902, 2866 (C–H); 1232, 1169, 1134 (C–O–C, C–F). ¹H NMR spectrum (CDCl₃), δ, ppm: 2.54–3.43 m (5H, CF₂CH₂, CH₂CHS), 3.54–3.91 m (4H, CH₂OCH₂), 4.29–4.44 m (1H, CHI). ¹⁹F NMR spectrum (CDCl₃), δ, ppm: 35.65–35.96 m (2F, γ -CF₂), 37.14–37.42 m (2F, β -CF₂), 46.74–49.47 m (2F, α -CF₂), 80.52–80.81 m (3F, CF₃). Found (%): C 25.12, H 2.14, F 35.86, S 6.64.

Poly{sulfanediyl[1-(2,2,3,3-tetrafluoropropoxy)methyl]ethylene]} (2e). A viscous oil of dark-brown color. IR spectrum, ν , cm⁻¹: 2998, 2927 (C–H); 1108 (C–F, C–O–C). ¹H NMR spectrum (CDCl₃), δ, ppm (J , Hz): 2.76–3.20 m (3H, CH₂CHS), 3.61–3.97 m (4H CH₂OCH₂), 5.93 t (1H, HCF₂, $J_{H,F}$ 53.2). ¹⁹F NMR spectrum (CDCl₃), δ, ppm: 21.15–23.21 m (2F, HCF₂), 36.71–37.50 m (2F, CF₂CH₂). Found (%): C 33.97, H 3.71, F 34.79, S 18.11.

CONCLUSIONS

(1) First the oligomers were synthesized based on the (polyfluoroalkyl)methyl oxiranes and thiiranes with molecular weights in the range of 1170–2300 g mol⁻¹.

(2) In testing oil I-20A with additives of the synthesized oligomers (0.5–2 wt %) according to GOST 9490-75 it was found that the weld load increases and the size of wear scar of the body rubbing decreases compared to the unmodified base oil. The sulfur oligomers are of the greatest positive tribological effect.

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