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Synthesis and properties of the ϵ -aminocaproic acid polyfluorinated oligomers

A.V. Miroshnichenko., A.I. Rakhimov, N.A. Rakhimova

Volgograd State Technical University, Russia, 400131, Volgograd, Lenin Prosp.,28
e-mail: organic@vstu.ru

Abstract: Oligomers of ϵ -aminocaproic acid with general formula $H-[HN-(CH_2)_5-C(O)]_m-OH$ ($m = 60-80$) were separated from the polycaproamide waste and were modified by the reactions with the polyfluorinated alcohols $H(CF_2CF_2)_nCH_2OH$ and polyfluoroalkyl chlorosulfites $H(CF_2CF_2)_nCH_2OS(O)Cl$, $n = 1, 2$. The study of properties of obtained products (solubility, IR-spectra, elemental analysis) has shown that the main reaction direction of oligomers with polyfluorinated alcohols is N-polyfluoroalkylation and in case with polyfluoroalkyl chlorosulfites O - polyfluoroalkylation. There were obtained the polyfluoroalkylated oligomers with the fluorine content - 0.29-6.67% and with the molecular mass from 4600 to 9500.

Keywords: Oligomers of ϵ -aminocaproic acid, polyfluoroalkyl chlorosulfites, polyfluorinated alcohols, polyfluoroalkylation, polyfluoroalcoholysis.

It is known that oligoamides, same as polyamides have a range of goodness, such as high adhesion properties, hydrophobic nature, nontoxicity, oil-and-petrol resistance, durability of the polymer products and covers. Besides that, the reactive end groups existence in the oligomers structure makes possible their modification, that allows to give it new useful properties. As it was shown [1,2], an introduction of polyfluoroalkyl groups increases the hydrophobic properties of the oligomeric coatings and decreases its' ability to inflammation. An addition of low-molecular polyfluoroalkylated oligomers in polycaproamide makes easier its processing and increases the durability [3].

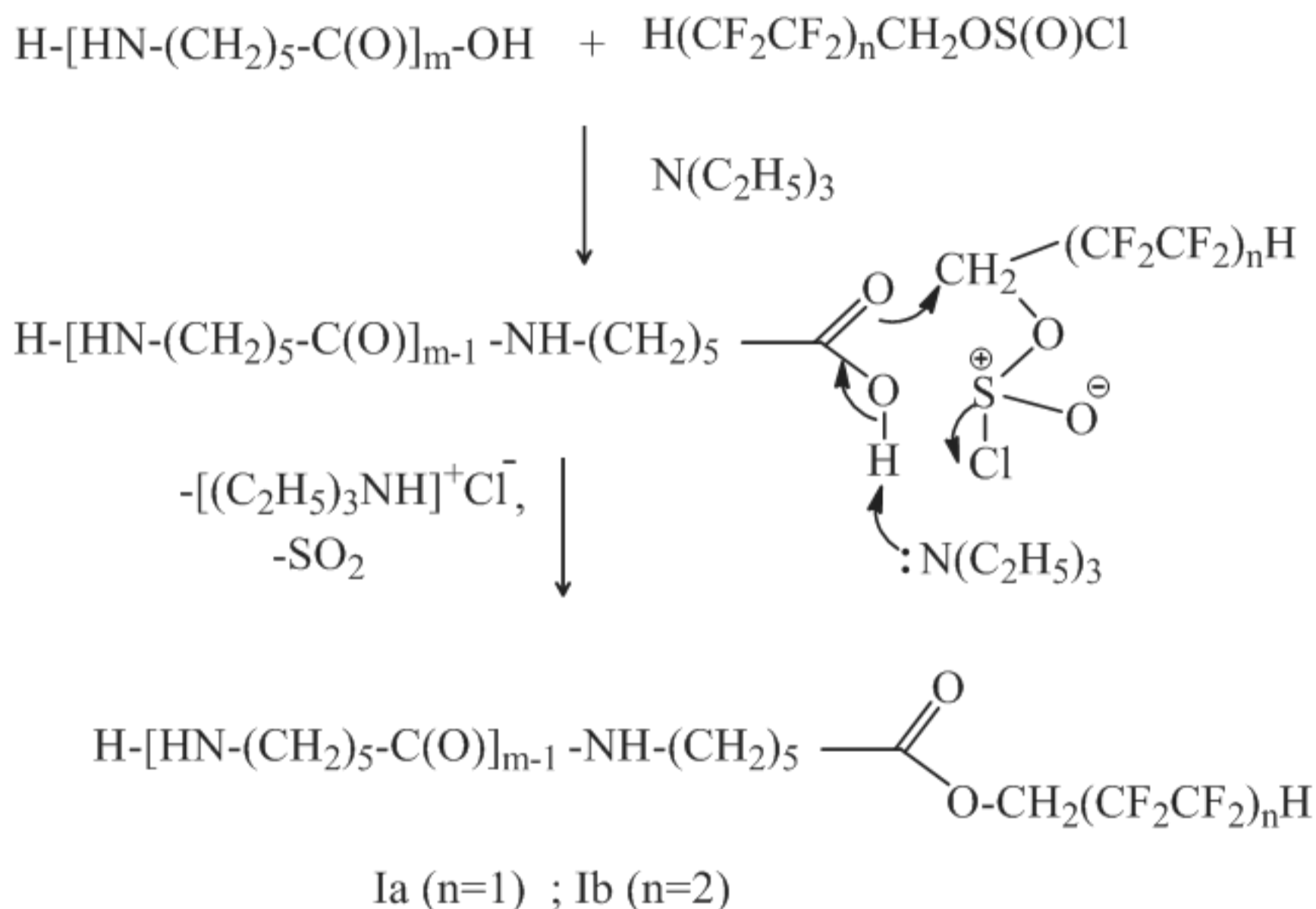
Earlier the polyfluoroalkyl ϵ -aminocaproic acid esters were achieved using the reaction of polyfluorinated alcohols with ϵ -caprolactam in conditions of catalysis by triethylamine and acids amides [2]. Using the calculative forecast method its biomedical activity summing up showed the high antiviral activity. The high antiviral activity of the oligomers of ϵ -aminocaproic acid was experimentally confirmed in the Research Institute of Influenza (Saint-Petersburg, professor Kiselev O.I.) [4].

In this regard, on account of the industrial accessibility of these oligomers, for us it seemed to be necessary to study the polyfluoroalcoholysis and polyfluoroalkylation of fractions of ϵ -aminocaproic acid soluble in water.

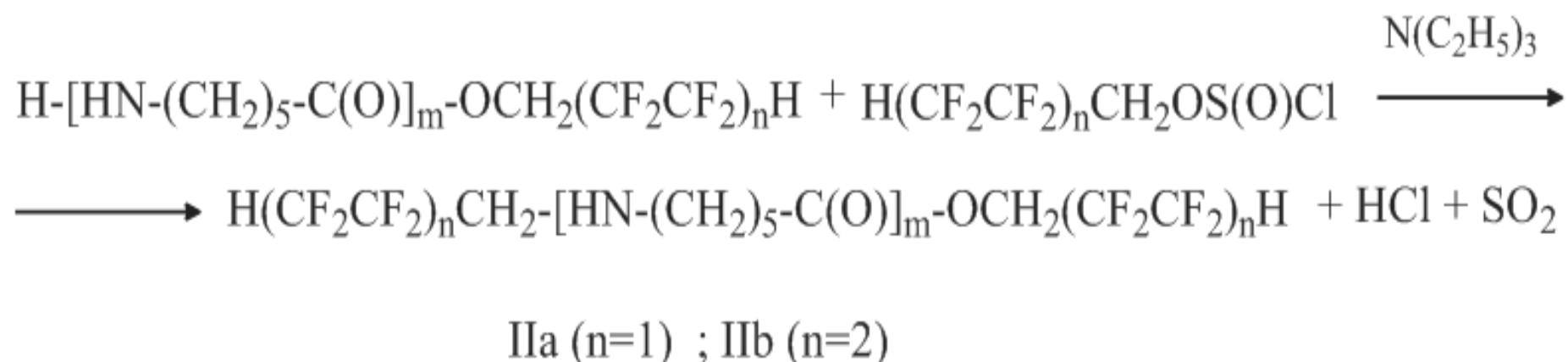
There oligomer group of general formula $H-[HN-(CH_2)_5-C(O)]_m-OH$ was separated from the water using the waste products recrystallization. According to the end groups amount it was defined that $m=60-80$. Further the oligomer was modified by the polyfluorinated alcohols $H(CF_2CF_2)_nCH_2OH$ and polyfluoroalkyl chlorosulfites $H(CF_2CF_2)_nCH_2OS(O)Cl$, $n = 1, 2$.

It is known that polyfluoroalkyl chlorosulfites are the high reactivity compounds, soft polyfluoroalkylation reagents for HO-alcohol group, phenols, carboxylic acids [5-8].

The polyfluoroalkyl chlorosulfites with oligomer reaction in the presence of triethylamine occurs in the soft conditions (the same for the carboxylic acids) and leads to the water soluble oligomers **Ia** and **Ib** formation. The six-membered polar intermediate state helps the nucleophilic substitution by reference to the α -methylene group polyfluoroalkyl chlorosulfites in the presence of carboxylic group:

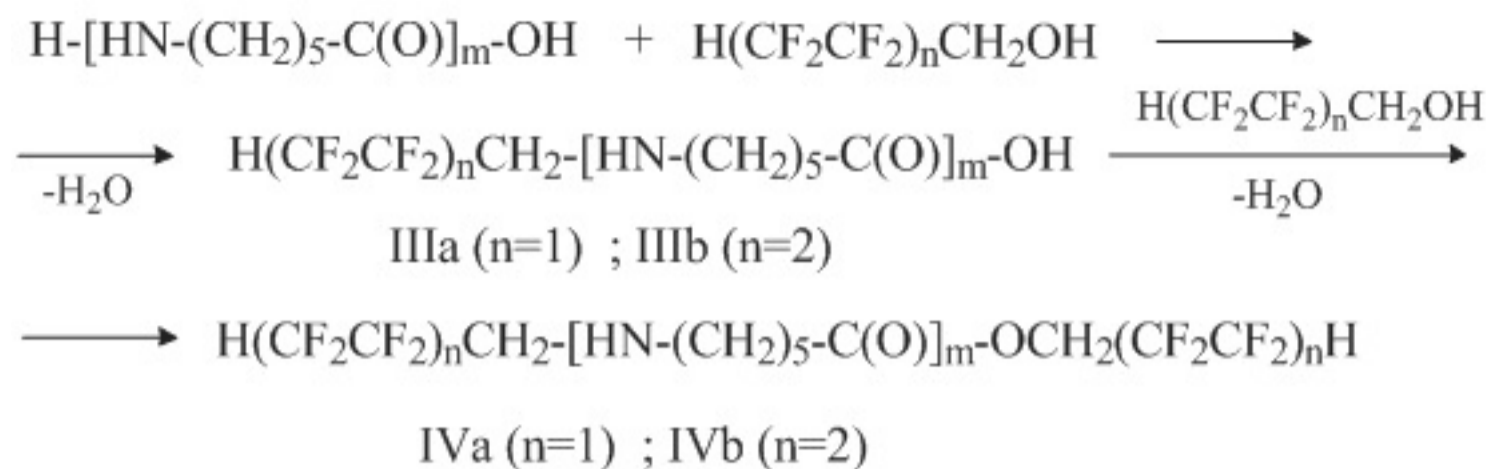


Further the reaction occurs with the water-insoluble N, O - di (polyfluoroalkyl) derivants of oligomers **IIa** and **IIb** formation:

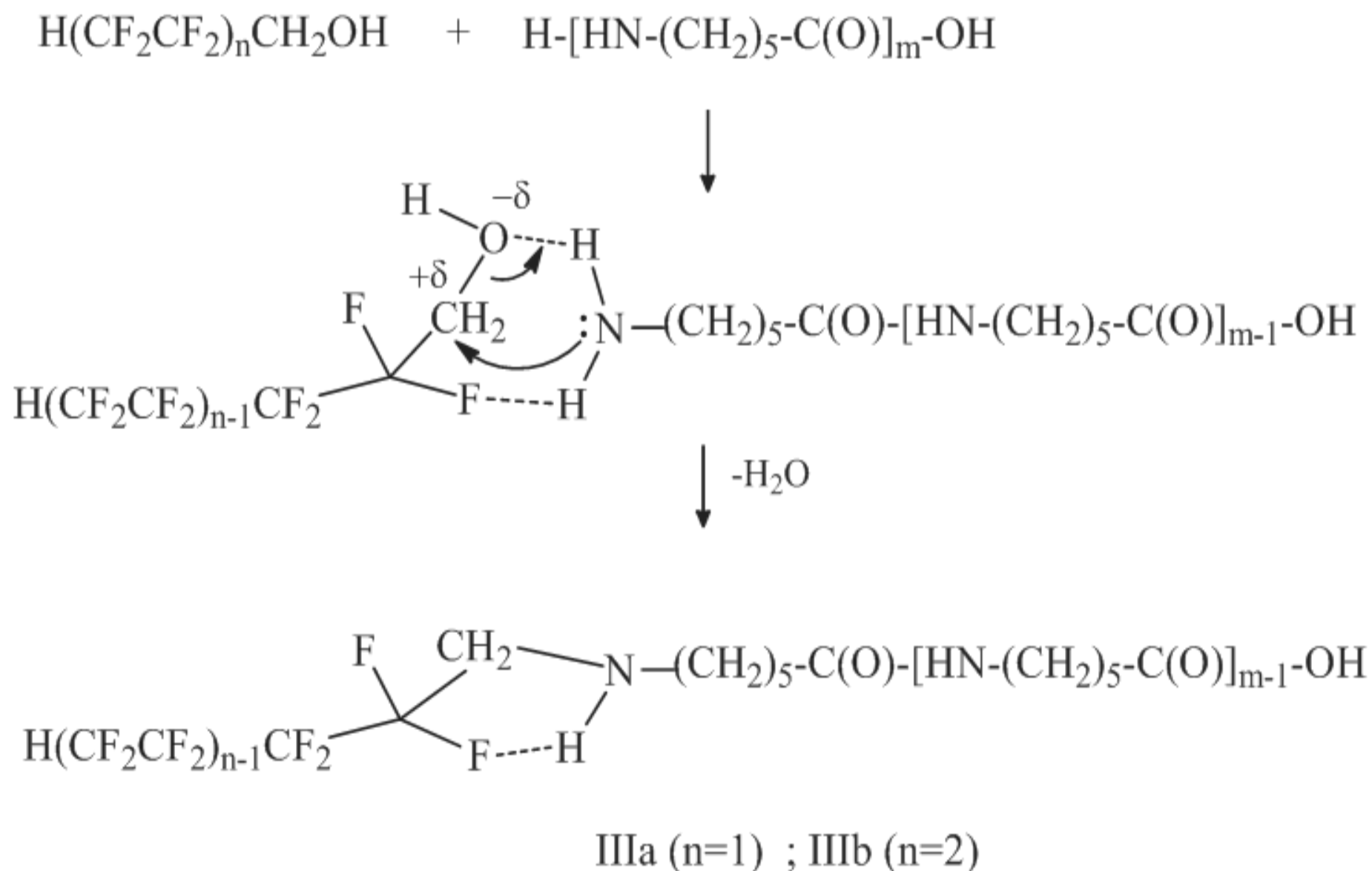


It seems that the oligocaproamide with the fluorinated alcohols reaction occurs in the

following way:



It is obvious that the mechanism of the N and O -polyfluoroalkylation of oligomer by the polyfluorinated alcohol is different from the mechanism of the reaction with polyfluoroalkyl chlorosulfite. The alcohol acidic nature and the low electron density at the oxygen atom of the HO-group makes the esterification of the oligomer's carbonyl group more difficult and the cooperation may proceed with the amide bond destruction (that is why the oligomers' III and IV molecular mass decreases), while the presence of the electrophilic center at the carbon atom CH₂ - group promotes the attack of lone-pair electrons on nitrogen atom of terminal NH₂ - group of oligomer's molecule of this center. This confirms the fact that the main product of the polyfluorinated alcohol with oligomer reaction is the product of mono-N-polyfluoroalkylation - (**IIIa**, **IIIb**). The formation of the intermolecular hydrogen bond -F ••• H- helps the transition structure stabilization:



Formulas and the molecular mass of the achieved oligomers are shown in Table 1.

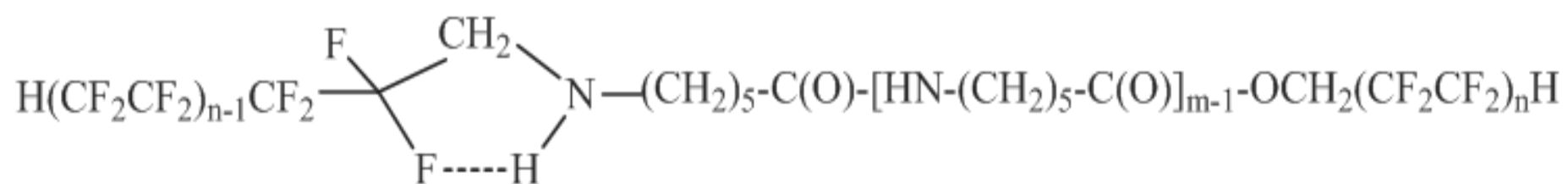
Table 1. The polyfluoroalkylated oligocaproamides.

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#	Formula	Molecular weight
Ia	H-[HN-(CH ₂) ₅ -C(O)] _m -O-CH ₂ CF ₂ CF ₂ H	7380
Ib	H-[HN-(CH ₂) ₅ -C(O)] _m -O-CH ₂ (CF ₂ CF ₂) ₂ H	9160
IIa	HCF ₂ CF ₂ CH ₂ -[HN-(CH ₂) ₅ -C(O)] _m -O-CH ₂ CF ₂ CF ₂ H	8350
IIb	H(CF ₂ CF ₂) ₂ CH ₂ -[HN-(CH ₂) ₅ -C(O)] _m -O-CH ₂ (CF ₂ CF ₂) ₂ H	9480
IIIa	HCF ₂ CF ₂ CH ₂ H-[HN-(CH ₂) ₅ -C(O)] _m -OH	7100
IIIb	H(CF ₂ CF ₂) ₂ CH ₂ -[HN-(CH ₂) ₅ -C(O)] _m -OH	6520
IVa	HCF ₂ CF ₂ CH ₂ -[HN-(CH ₂) ₅ -C(O)] _m -O-CH ₂ CF ₂ CF ₂ H	6130
IVb	H(CF ₂ CF ₂) ₂ CH ₂ -[HN-(CH ₂) ₅ -C(O)] _m -O-CH ₂ (CF ₂ CF ₂) ₂ H	4560

The polyfluoroalkylated oligomers construction was researched using the IR-spectroscopy. The characteristic frequencies of absorption in the IR-spectra of the starting and polyfluoroalkylated oligomers are shown in the table 2.

In the large wave numbers range 3571-3272 cm⁻¹ there was marked an intensive absorption band for the amides NH-groups with the frequency 3284-3272 cm⁻¹, that according to its location and intensity changes in the small ranges. The absorption band 3116 cm⁻¹ in the starting oligomer has the medium intensity. The analogical absorption is observed in the interval 3072-3066 cm⁻¹ in the non-soluble in hot water oligomers **IIa**, **IIb** and **IVa**, **IVb**. The absorption band displacement is resulted from the NH-group association, which appears during the process of polyfluoroalkylation of the final oligomer's NH₂ - group with the fluorine atoms by the nearest CF₂ - group:

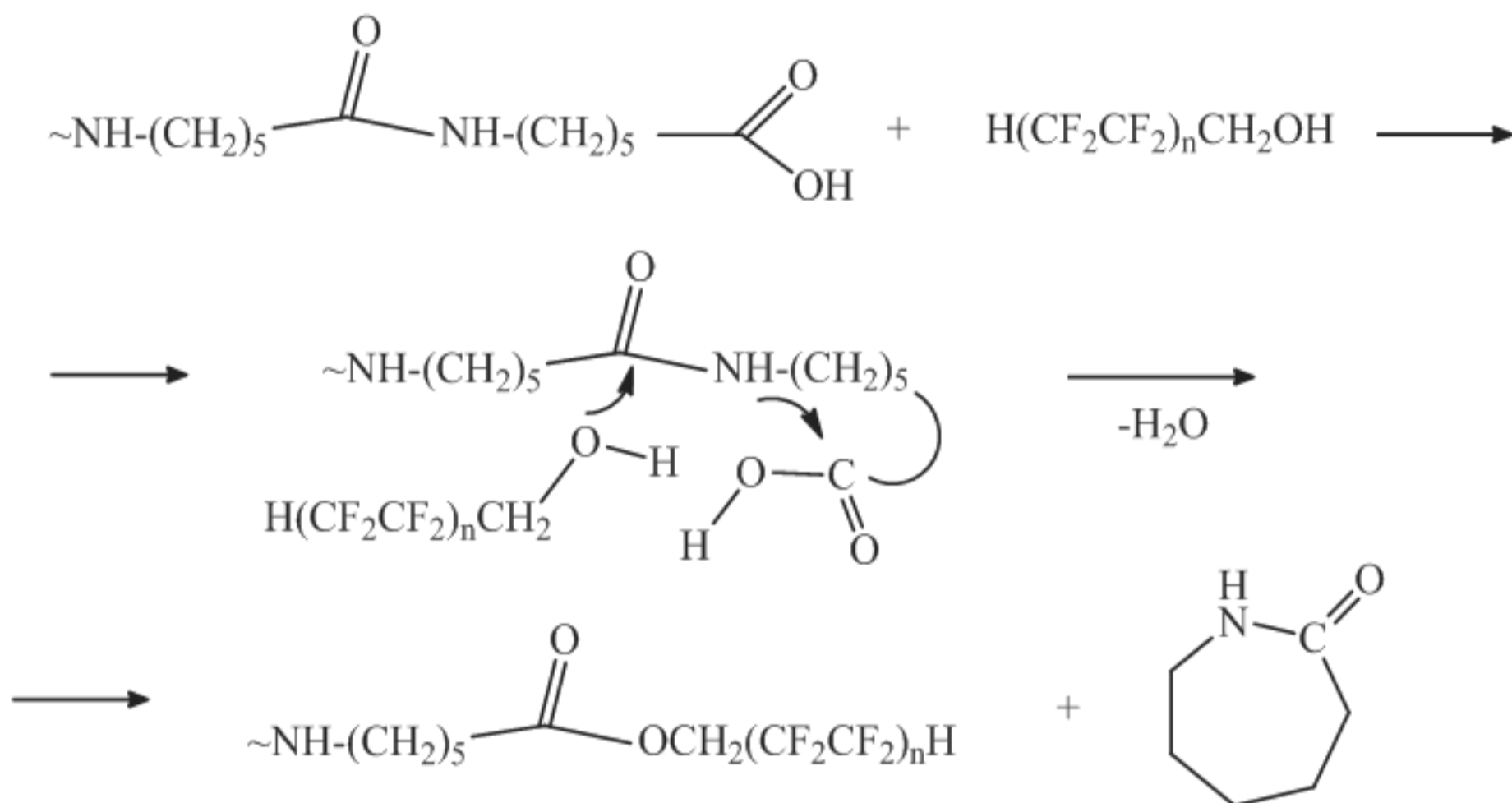


The 1176 cm⁻¹ absorption band, which complies with asymmetrical deformation vibration of the C-F bond is the demonstration of the H(CF₂CF₂)₂CH₂ - group presence in the oligomer's molecules (with exception of the fluorine molecule content). The absence of the CF₂ - group association with H-N-group hydrogen atom in the oligomers **Ia** and **Ib** results in

this absorption band displacement to the large wave numbers (1184 cm^{-1}).

The presence of the ester group in the oligomers **Ia**, **Ib** and **IIa**, **IIb** is obvious because of its absorption in the stretch vibration sphere of the ester group with $\nu_{\text{C=O}} = 1748\text{-}1752\text{ cm}^{-1}$.

The difference of the fluorine content for the water soluble oligomers **II** and **IV** is attributable to their different molecular mass that is connected to the reaction polyfluorinated alcohol along the starting oligomer amide groups. The high fluorine content 5,48-6,67% in the oligomer **IV**, which was achieved by boiling in the polyfluorinated alcohol and therefore it's lower molecular mass (4500-6100) is explained by alcoholysis of oligomer with amide bond destruction and ϵ -caprolactam or cyclic oligomers formation:



Polyfluoroalkylated oligomers **I**, **III** are white, crystal compounds, that are water soluble (fluorine content 1.03-1.66 and 1.07-2.33% accordingly). Increase of fluorine content in oligomers **II** and **IV** (1.82-6.67%) decrease its water solubility. Such oligomers is recommended for testing in the industrial rubber products for the purpose of decrease defacement while exploitation.

After the insoluble in the boiling water oligomer and the one dropping out while cooling till $20\text{ }^\circ\text{C}$ were separated, from the water supernatant liquid after its concentration also drops out the oligomer that contents a small fluorine amount (0.29-1.0%). On the one hand the good water solubility can be explained by the presence of the cyclic oligomers, that are good water soluble and sublimating at high temperature, on the other hand, the low molecular oligomers with $n \leq 20\text{-}30$ are good water soluble. The fluorine presence in this product lets to suggest that the product consists of polyfluoroalkylated through the amino group low molecular oligomer (the free carboxylic group helps its solubility) and of the cyclic non fluorinated oligomer.

Experimental.

The structure of the compounds obtained was confirmed by IR spectroscopy. The IR spectra

were recorded on a Spekord - M82 instrument, in the suspension with the paraffinic oil.

1. The oligomeric waste of polycaproamide manufacture separation

The oligomers' waste was powdered, treated by water at the temperature 20-25°C and then easily soluble ε-caprolactam and low molecular oligomers were separated. The cyclic oligomers were extracted using ethanol. The residue was boiled in the water and filtered at the temperature 80-90°C. The white, crystal oligocaproamide precipitated from the filtrate after cooling. Using the potentiometric titration method of the final H₂N - and HOOC - groups it was defined that oligocaproamide H[HN(CH₂)₅C(O)]_mOH has average m=60-80.

2. Oligocaproamide polyfluoroalkylation by the 1,1,5- trihydroperfluoropentyl chlorosulfite in the presence of triethylamine

In a reactor provided with a stirrer, thermometer, reflux condenser was put 2,5 g. (0.27·10⁻³ mole) of oligomer, 0.6 ml (0.004 mole) of triethylamine and 15 ml of chloroform, the reaction mixture was cooled to -10°C and maintaining the temperature, the solution of 2.18 g (0.004 mole) 1,1,5- trihydroperfluoropentyl chlorosulfite in 5 ml of chloroform was fed. Then the temperature was slowly raised to 60-65 °C and exposed while stirring during 2 hours. The oligomeric product was filtered, washed with chloroform and recrystallized from the water. There was obtained: water insoluble product (**IIb**) 0.39 g, (15.6 %), MP 220-228°C, fluorine content 3.19 %; water soluble product (**Ib**) 0.93 g. (37.2 %), MP 225-227°C, fluorine content 1.66 % .

The reaction with 1,1,3- trihydroperfluoropropyl chlorosulfite was carried out similar, the results are shown in the Table 2.

3. The polyfluoroalkylation of oligocaproamide by the 1,1,5-trihydroperfluoropentan-1-ol

In a three-necked reactor provided with a stirrer, thermometer, reflux condenser was put 8 ml (0.05 mole) 1,1,5- trihydroperfluoropentan-1-ol and 4.95 g. (0.54·10⁻³ mole) of oligocaproamide. The reaction mixture was heated to boiling and allowed during 12 hours. After the reaction mixture was cooled, it was diluted with 20 ml of acetone. The precipitated white substance was filtered, and using the boiling water soluble part was extracted. The water insoluble oligomer **IVb** in amount of 0.59 g. (11.9 %) with MP 215-220 °C and the fluorine content - 6.67 % was obtained. After cooling water solution 2.26 g. (45.7 %) of oligomer **IIIb** with MP 232-240 °C and fluorine content equal to 2.33 % was obtained. The reaction with 1,1,3- trihydroperfluoropropan-1-ol was carried out similar, the results are shown in the Table 2.

Table 2. Physico-chemical properties of the initial and polyfluoroalkylated oligomers.

No	Olygomer	Yield, %	MP, °C	Content of Element, %		Solubility in boiling water	The charact	
				N	F		NH amido group	↑ (NI ar
1	initial	-	220-222	12.2	-	soluble	3284	(

2	Ia	24.8	235-240	12.1	1.03	soluble	3286	3
3	Ib	37.2	227-235	12.0	1.66			
4	IIa	10.0	230-235	9.9	1.82	insoluble	3271	3
5	IIb	15.6	220-228	9.8	3.19			
6	IIIa	45.6	230-235	11.8	1.07	soluble	3280	3
7	IIIb	45.7	232-240	10.9	2.33			
8	IVa	13.2	235-245	8.9	2.48	insoluble	3280	3
9	IVb	11.9	215-220	9.9	6.67			

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Recommended for publication by Prof. A. I. Rakhimov