



**АКАДЕМИЯ НАУК РОССИЙСКОЙ
ФЕДЕРАЦИИ**

**Институт органической химии им. Н.Д.
Зелинского РАН**

**Олигомеры и полимеры с
перфторалкиленоксидными
звеньями**

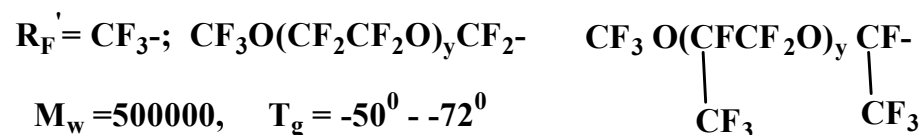
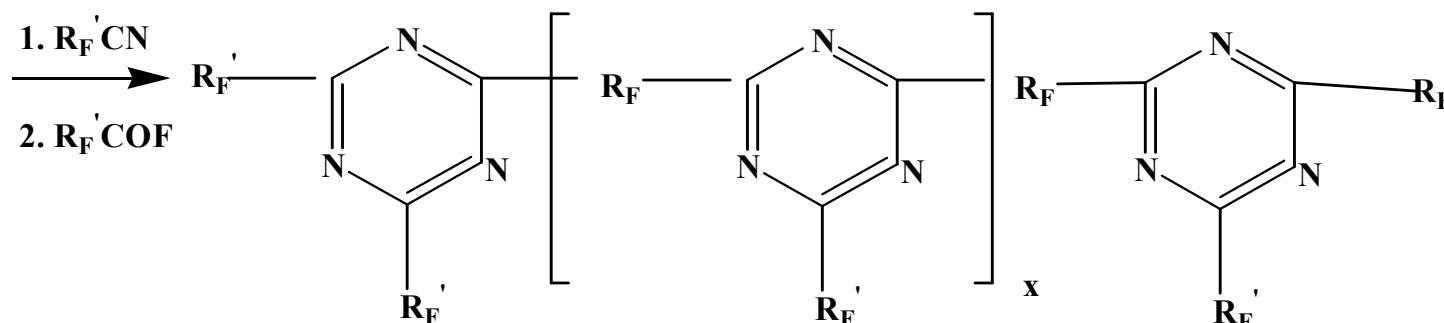
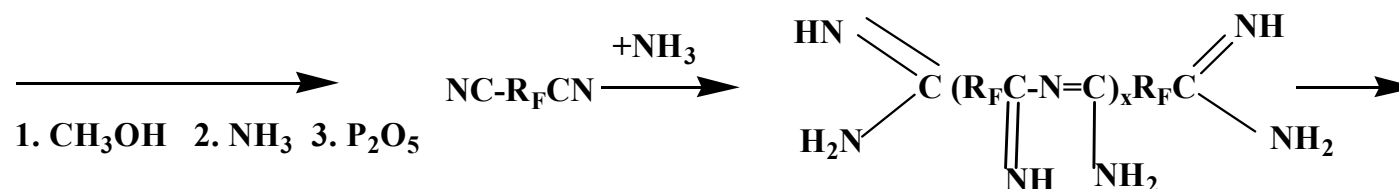
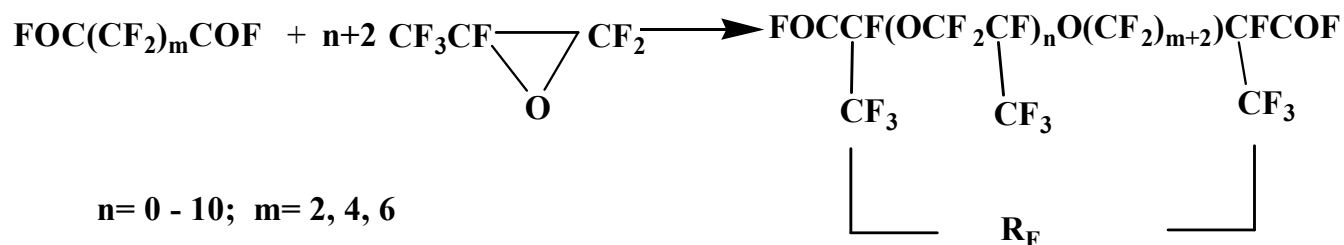
С.П. Круковский, А.А. Ярош, А.М. Сахаров



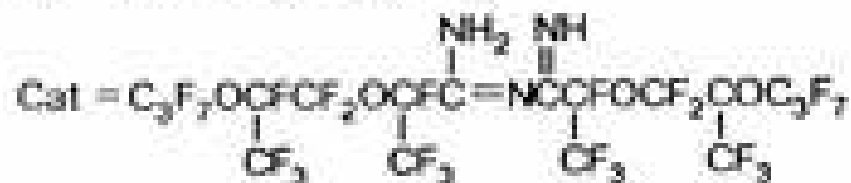
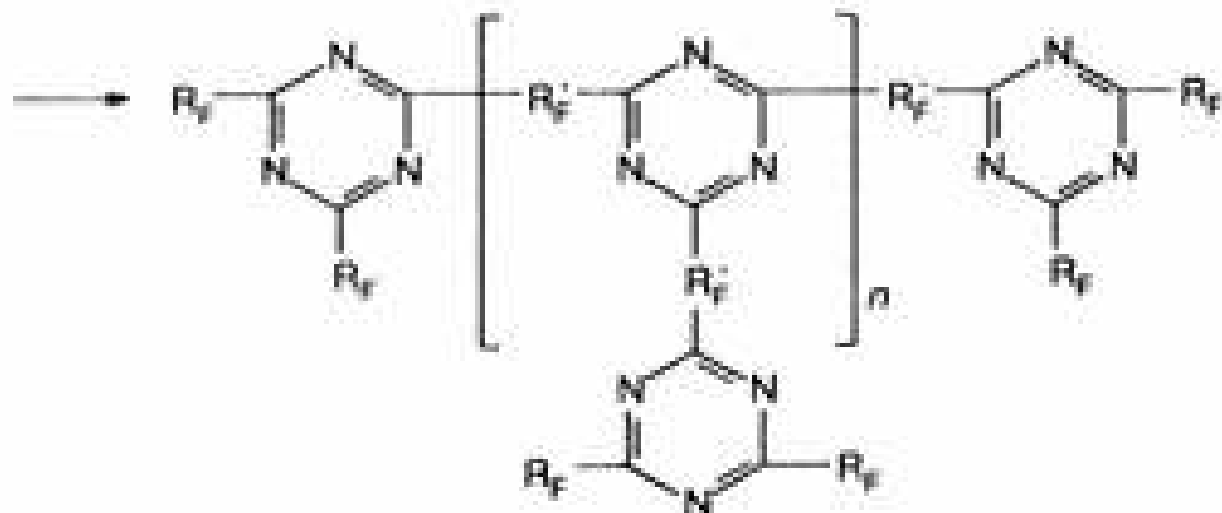
RUSSIAN ACADEMY OF SCIENCES
Zelinsky Institute of Organic Chemistry

- Oligomers and polymers with perfluoroalkyleneoxide links
- S.P. Krukovsky, A.A. Yarosh and A.M. Sakcharov

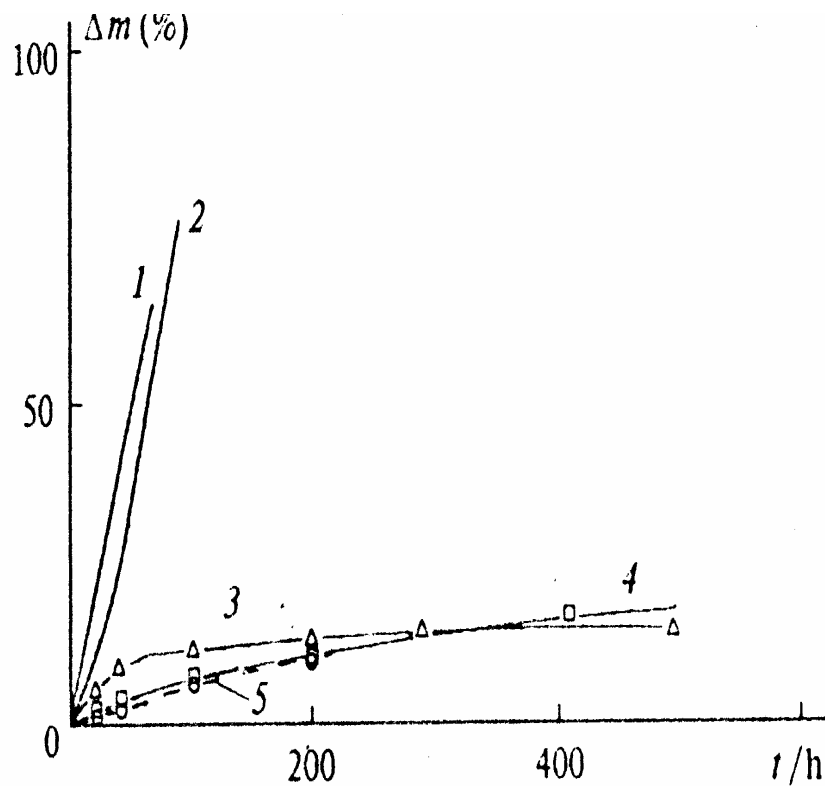
Synthesis of polyperfluorotriazines



Co-trimerization of mono- and dinitriles of perfluorocarboxylic acids under high pressure



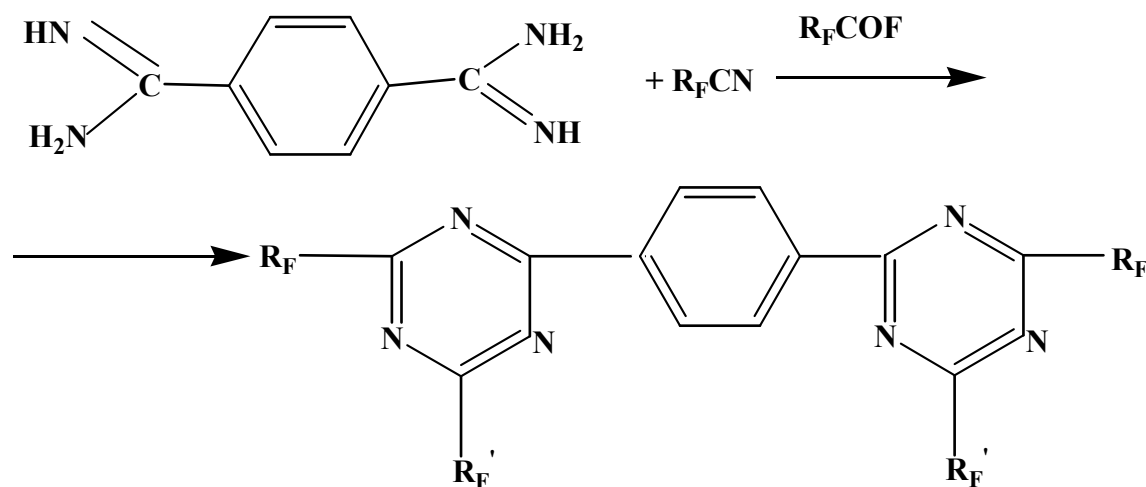
Weight loss (Δm) of perfluoropolyethers (PFPE) in the presence of steel-45 at 200°C



- 1 and 2 - perfluoropolyethers without stabilizers (oligoperfluoropolytriazine)
- 3 and 4 - perfluoropolyethers in the presence of 5% (w/w) oligoperfluoropolytriazine
- 5 – perfluoropolyether without stabilizer and the metal



Perfluorooxyalkylene triazinyl benzenes



R_F and $R_F' = CF_3O(CF_2O)_a(CF_2CF_2O)_bCF_2-$; $a/b = 3-7: 1$
 $CF_3O(CF_2O)_5CF_2-$

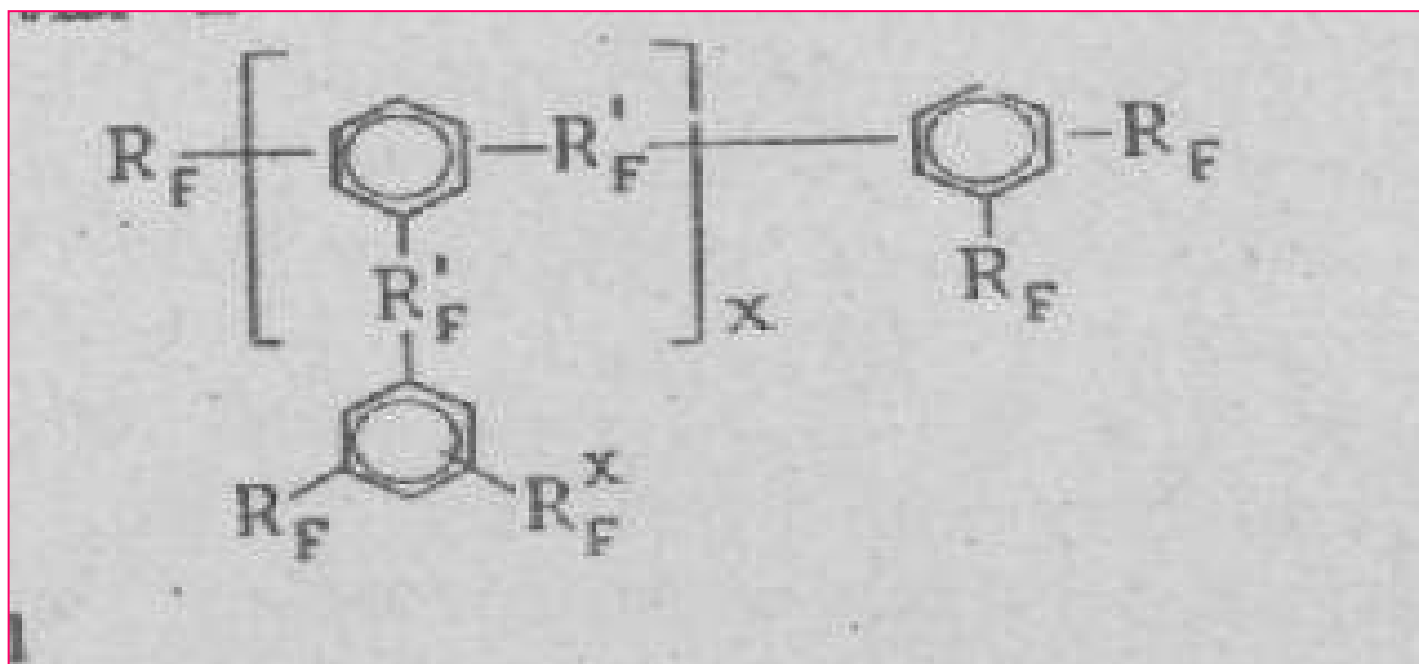
$M_n = 2000 - 43500$ $T_g = -135^\circ C$ Weight loss at $300^\circ C$ for 30 h <6%

Oligoperfluoroalkylene benzenes

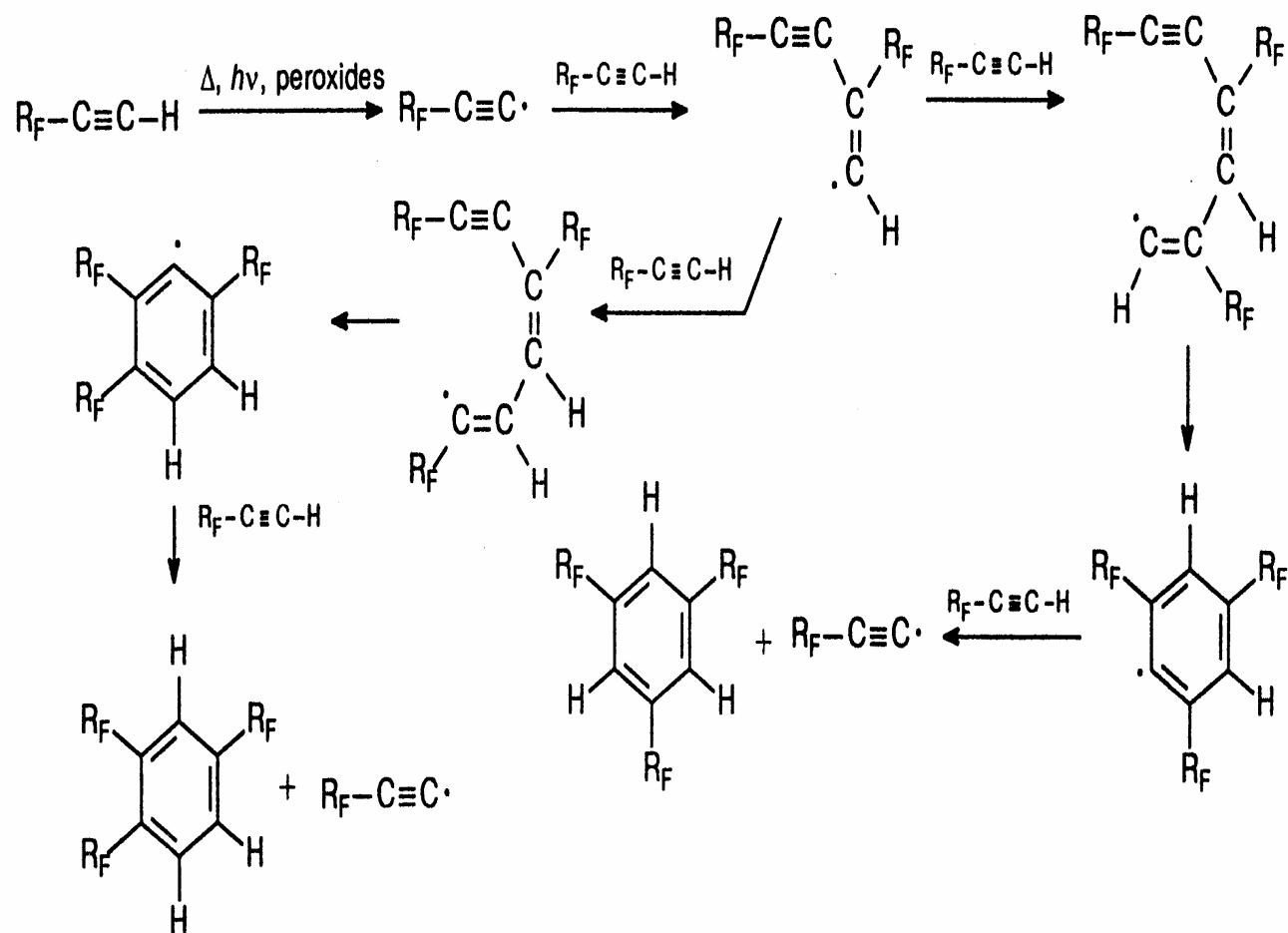
$R_F' = -(CF_2)_6-$; $R_F = CF_3O(CF_2CF_2O)_{2-5}CF_2-$

$M_n = 4000 \div 8000$ $T_g = -40^{\circ}C \div -96^{\circ}C$;

$T^{10\%} = 400-425^{\circ}$



Peculiarities of cyclotrimerization of perfluoroalkylacetylenes



Cross-linked polymers containing –CF₂O- and –CF₂CF₂O- links in the chain

- $\text{CF}_2=\text{CF}-\text{CF}=\text{CF}_2 + \text{CF}_3(\text{CF}_2\text{O})_x (\text{CF}_2\text{CF}_2\text{O})_y\text{-A-} (\text{CF}_2\text{O})_x (\text{CF}_2\text{CF}_2\text{O})_y\text{CF}_2\text{COF}$
- $M_n = (1.4-2.7) \times 10^4 ; x/y = 5-10 / 1$
- (180-220° C Active oxygen 0.6-1.1 weight %)
- $\text{-----} \rightarrow \sim (\text{CF}_2\text{O})_x (\text{CF}_2\text{CF}_2\text{O})_y \text{CF}_2 \sim$
- $\quad \quad \quad |$
- $\quad \quad \quad \sim \text{CF}-\text{CF} \sim$
- $\quad \quad \quad |$
- $\quad \quad \quad \sim (\text{CF}_2\text{CF}_2\text{O})_y (\text{CF}_2\text{O})_x \text{CF}_2 \sim$
- (gel-fraction 85%).
- A – peroxide links: $\text{OCF}_2\text{OOCF}_2\text{O-}; \text{OCF}_2\text{CF}_2\text{OOCF}_2\text{CF}_2\text{O-};$
 $\text{OCF}_2\text{OOCF}_2\text{CF}_2\text{O-}$

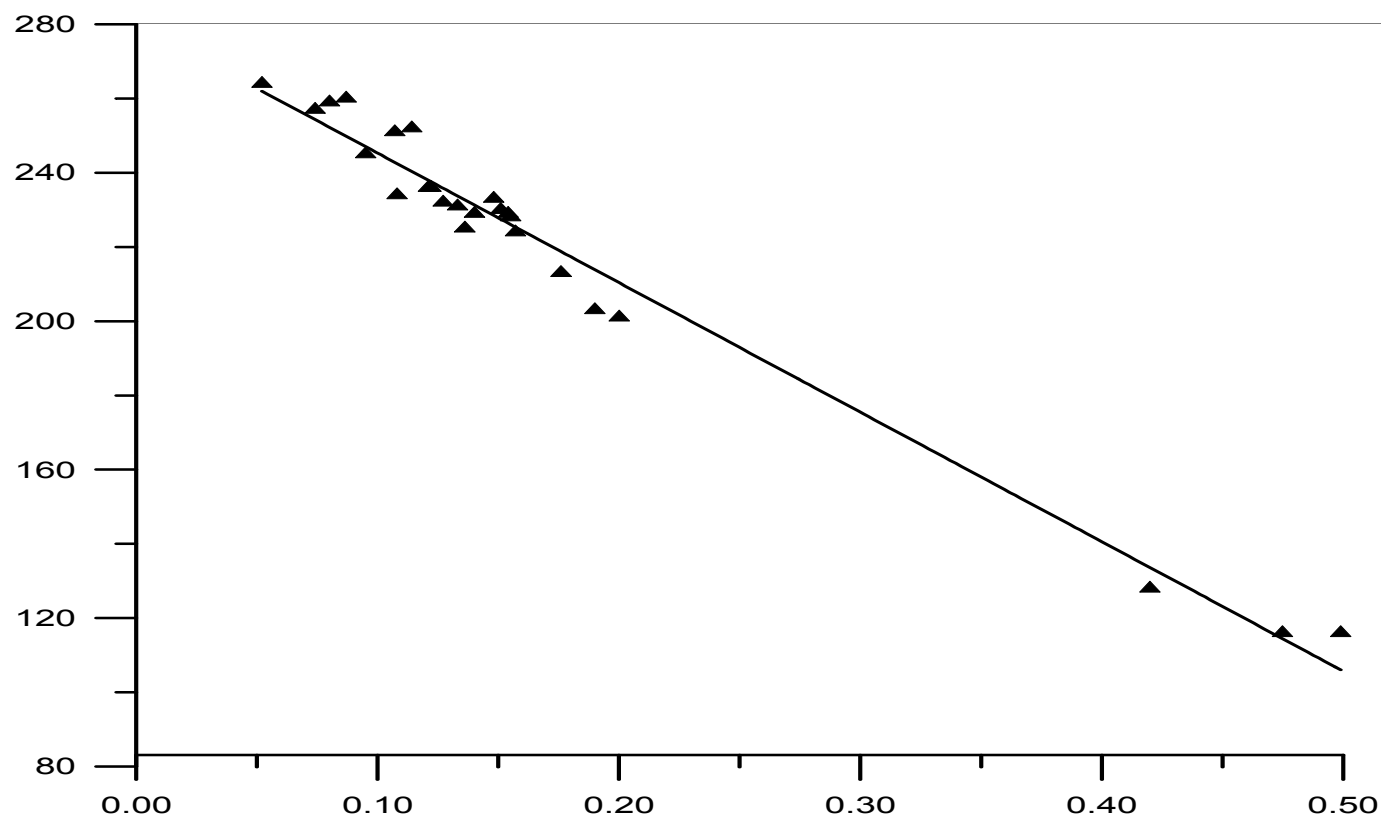
Cross-linked polymers containing –CF₂O- and –CF₂CF₂O- links in the chain

Oligomers with reactive groups	M _n	T _g , °C
<p>NC(CF₂O)_x (CF₂CF₂ O)_yCF₂ CN (80 mol.%)</p> <p>CF₃(CF₂O)_x(CF₂CF₂O)_yCF₂CN (20 mol.%)</p> <p>Mix of mono- and dinitriles; x/y = 21/4</p>	2700	-(140-145°C)
<p>[(CF₂O)_x O₂ (CF₂CF₂O)_y]_n x/y = 21/4 ; Act. Oxygen 0.8%</p> <p>CF₂=CF-CF=CF₂</p>	4800	-(140-145°C)

Glass transition temperature (T_g) vs ratio O/F in perfluoropolyethers

T, g (K)

$T, g = 283 - 370$ a

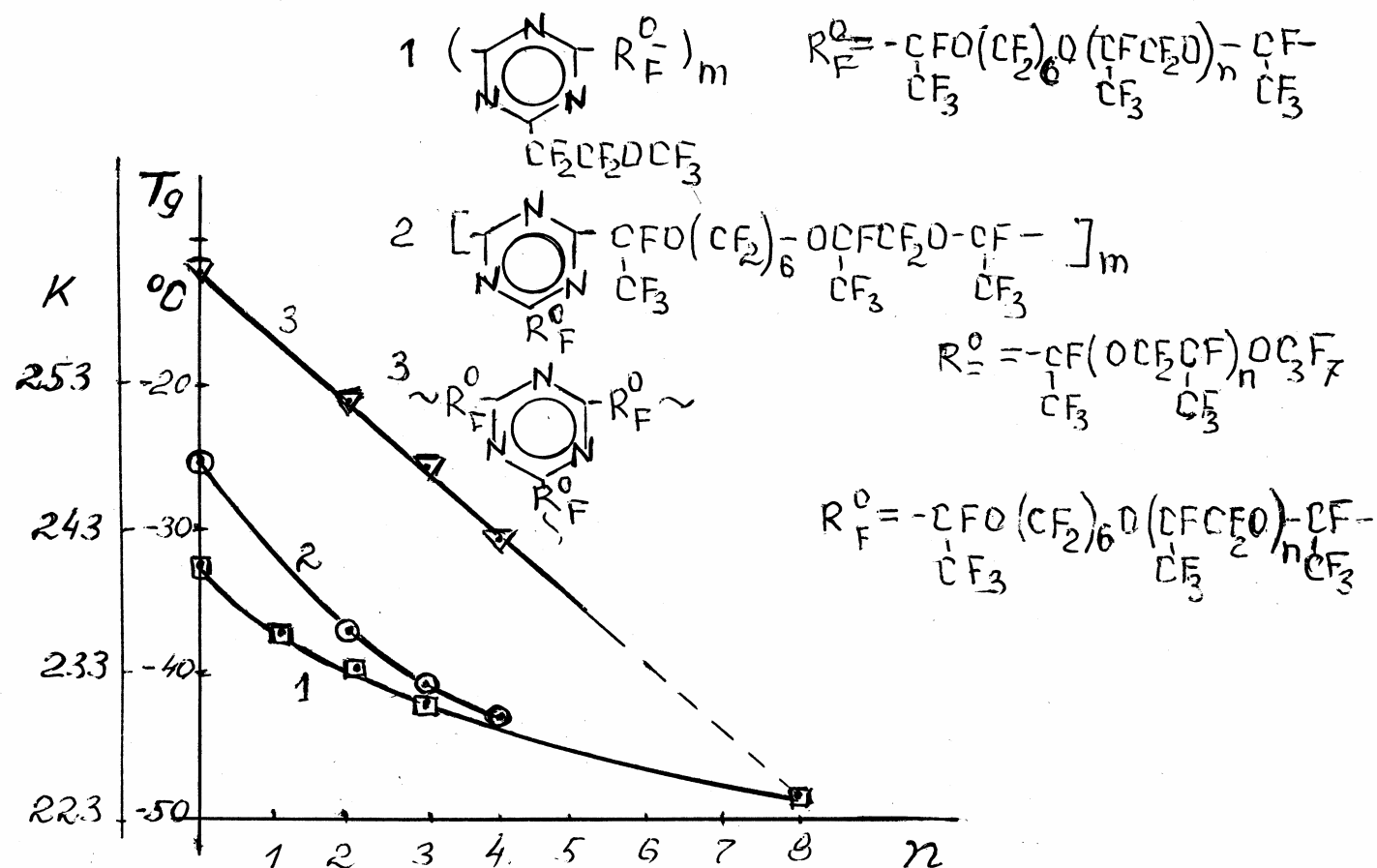


$a = O/F$

Unit	-[CF(CF ₃)CF ₂ -O-]	[- CF ₂ CF ₂ -O-]	[-CF ₂ -O-]
$a = O/F$	0.167	0.250	0.500
T_g, K (T_g, C)	221(-52)	191 (-82)	98 (-175)



Glass transition temperature (T_g) of linear and cross-linked polyperfluorooxyalkylene triazines vs the chain length of initial dinitriles



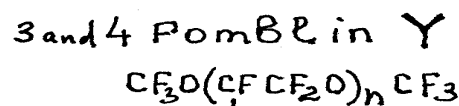
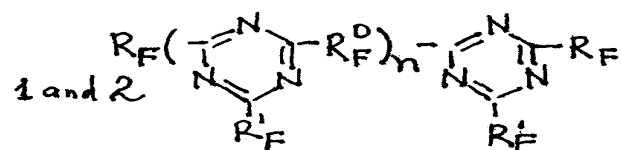
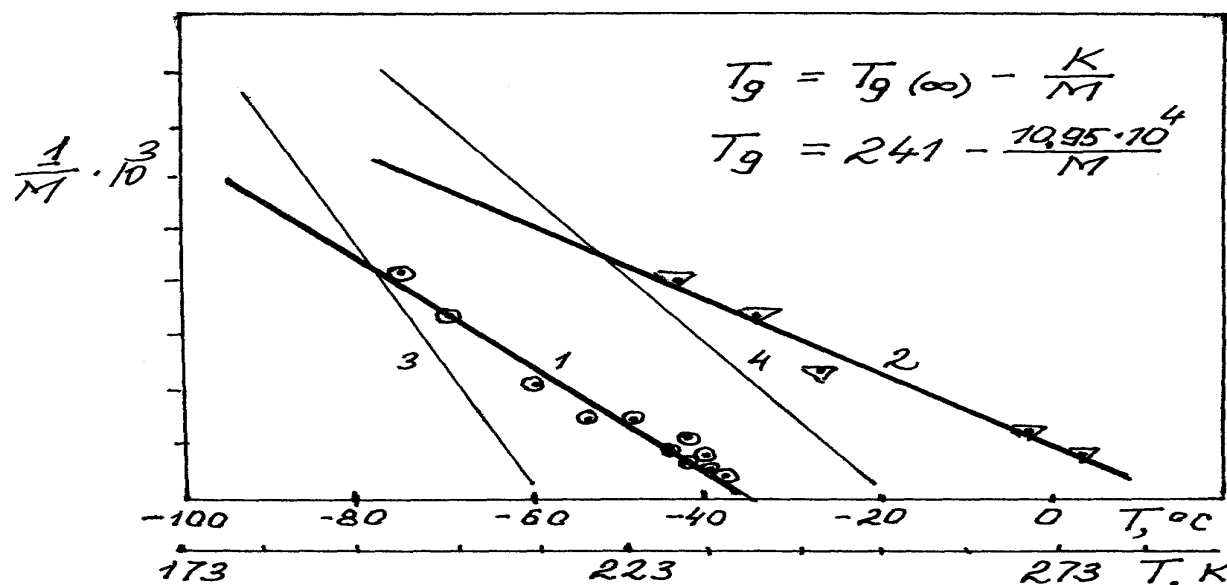
Glass transition temperature of cross linked (T_g ,) and linear (T_g)_o perfluoropolytriazines synthesized starting from dinitriles

$$\text{N}\equiv\text{CCF}(\text{CF}_3)\text{O}-(\text{CF}_2)_6-\text{O}-[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}(\text{CF}_3)\text{C}\equiv\text{N};$$

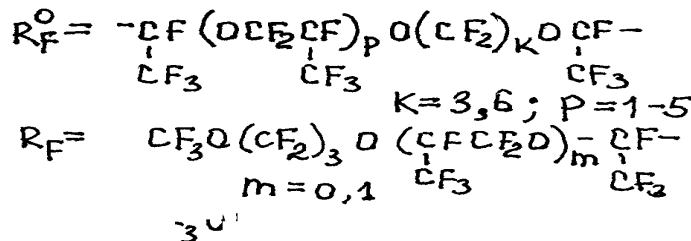
$$P_c - \text{number of atoms in the main chain}$$

n	T_g, °C (K)	T_{go}, °C, (K)	$T_g - T_{go}$	$P_c = \frac{2 T_{go}}{T_g - T_{go}}$	P_c (THEOR)
0	-12 (261)	-32 (241)	20	24.10	10
1	-16 (256)	-37 (236)	20	23.60	13
2	-21 (252)	-39 (234)	18	26.00	16
3	-25 (248)	-42 (231)	17	27.18	19
4	-31 (242)	-43 (230)	12	38.30	22

Glass transition temperature (1,3) and freeze temperature (2,4) of polyperfluorooxyalkylene triazine oligomers and “Fomblin Y” vs their molecular weight



$$n=8-25; M_n=(1,45-4,35) \cdot 10^3$$



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