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## Forecasting Glass Transition Temperatures of Fluorocontaining Polymers

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**Abstract:** The analysis of  $T_c$  ( $T_g$ , Glass Transition Temperature) dependence on both length and structure of the chain connecting triazine rings in perfluorinated polymers synthesized by the authors made it possible to improve the algorithm for  $T_c$  calculation developed earlier by A.A.Askadskii and G.L.Slonimsky. The proposed variant of  $T_c$  calculation allows reliable forecasting of cold resistance behaviour of both carbochain- and heterochain-fluoropolymers and tailoring of promising materials with the best properties.

**Keywords:** fluoropolymers, structure - glass transition temperature, calculation of glass transition temperature, tailoring of advanced structures.

The synthesis of polymers with pre-designed structures is among of the modern chemistry and physics challenges. The Glass Transition Temperature ( $T_c$ ) is one of the most significant polymer properties.  $T_c$  forecasting prior to the polymer synthesis, and reasoning from the chemical structure of its repeating units seems to be a topical problem. A considerable number of studies have already been devoted to the problems of  $T_c$  relation to the polymer chemical structure. In general, those calculations based on the assumption that the macromolecule repeating unit may be divided into a number of atomic groups with additive contributions to  $T_c$  independent of the environment. Its mathematical expression is as follows:

$$T_c \sum_i S_i = \sum_i S_i T_{ci} ; \quad T_c = \frac{\sum_i S_i \cdot T_{ci}}{\sum_i S_i} ,$$

Here  $T_{ci}$  is characteristic contribution of a group into  $T_c$ ; and  $S_i$  is the mass coefficient assigned to the group.

In the most of polymers  $T_c$  is estimable with accuracy  $\pm 20$  K. The methods for the  $T_c$  calculation based on such assumption was considered in [1-5] along with some other methods. However, the main disadvantages of the techniques offered by those authors are their non-flexibility and low accuracy. Another method different from those mentioned was introduced by A.A.Askadskii and G.L.Slonimsky for the calculation of  $T_c$  in amorphous polymers [6]. Basing on the temperature dependence of polymer packing factor they derived an equation that relates the polymer  $T_c$  to some parameters of the chemical structure of a macromolecule repeating unit:

$$\lg T_c = \frac{\sum_i K_i^x}{N_A \cdot \sum_i \Delta V_i} + A, \quad (1)$$

$\sum_i \Delta V_i$  is the characteristic mole volume of the repeating unit made up of the volumes of atoms that enter into the composition of the repeating unit (Van der Waals volume);

$\sum_i K_i^x$  - is an additive value (with volume dimensionality) related to the packing factor and to the coefficient of volumetric expansion of the polymer body (efficient volume of the chain repeating unit);

$N_A$  is Avogadro constant equal to  $6.023 \cdot 10^{23}$ ;  
 $A$  is a parameter of any linear polymer equal to 1.435.

The computation  $\sum_i \Delta V_i$  is based on the assumptions suggested in [7].  $\sum_i K_i^x$  is a sum of values  $K_X^j$  that characterize each element and every type of intermolecular interactions. The solution of a redundant equation system based on (1) resulted in  $K_X^j$  values shown in table 1.

**Table 1.** Numerical values for  $K_X^j$  [6].

#	Element or type of intermolecular interaction	Conventional sign	Numerical value (cm <sup>3</sup> /mole)
1	Carbon	$K_C^X$	10.739
2	Oxygen (>C=O)	$K_O^X$	3.925
3	Hydrogen	$K_H^X$	-1.248
4	Nitrogen	$K_N^X$	9.520
5	Chlorine	$K_{Cl}^X$	7.242
6	Hydrogen bond	$K_h^X$	7.338
7	Dipole-dipole interaction*	$K_d^X$	7.827
8	Coefficient of symmetry**	$K_n^X$	10.500

\* –  $K_d^X$  introduced in vinyl polymers when hydrogen in its main or side-chain is substituted with a radical of any type except phenyl.

\*\* –  $K_n^X$  introduced in case that all aromatic cores in the main-chain are substituted in n-position.

In further studies [8, 9] two more increments were added: main-chain oxygen  $K_{OO}^X$  equal to minus 5.244, and main-chain nitrogen  $K_{NO}^X$  that is 2.185.

In [10] the computation scheme was further improved to determine  $T_c$  in fluoropolymers (mainly, perfluorinated triazine polymers, PFT). To this end some novel  $K_X^j$  were introduced, their numerical values were determined (Table 2) and  $T_c$  were calculated in a number of polymers.

**Table 2.** Numerical values for  $K_X^j$  [10]

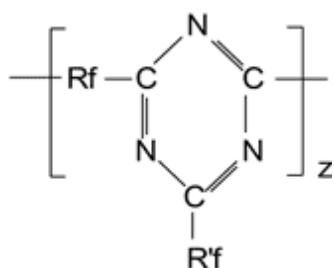
#	Element or type of intermolecular interaction	Symbol	Numerical value (cm <sup>3</sup> /mole)
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1	Fluorine	$K_F^X$	2.944
2	Oxygen (in chain)	$K_O^X$	0.215
3	Dipole-dipole interaction due to $\equiv\text{CF}$ group		2.080
4	Dipole-dipole interaction due to $-\text{CF}_2-$ group	$K_{d1}^X$	3.312
5	$\Delta$ Dipole-dipole interaction due to $-\text{CF}_3$ group	$K_{d2}^X$	3.610
		$K_{d3}^X$	

For homotypic PTF polymers with hexafluoroethylene oxide (HFPO) in their main or side chains the calculated  $T_c$  deviated from its experimental value less than by 2%. However, PFT polymers with tetrafluoroethylene oxide (TFEO) links in their main chains and most of synthesized PFT do not fit in the above calculation scheme.

In table 3 experimental  $T_c$  values for some polymers synthesized by us are compared to  $T_c$  calculated using the published data [10].

**Table 3.** Experimental and calculated  $T_c$  in polymers.



#	Rf	R'f	$T_c$ (K) [11]	$T_c$ (K) <i>calculated</i>
1	$-\text{CF}_2\text{OCF}_2\text{CF}_2(\text{CF}_2\text{OCF}_2)_2-$	$\text{CF}_3-$	207.5	234.5
2	$-(\text{CF}_2\text{OCF}_2)_2\text{CF}_2(\text{CF}_2\text{OCF}_2)_2-$	$\text{CF}_3-$	198	224
3	$-(\text{CF}_2)_6-$	$\text{C}_3\text{F}_7\text{OCFCF}_2\text{OCF}-$ <div style="display: flex; justify-content: center; gap: 20px; margin-top: 5px;"> <div style="text-align: center;">  CF<sub>3</sub></div> <div style="text-align: center;">  CF<sub>3</sub></div> </div>	237	255.5
4	$-(\text{CF}_2)_6-$	$\text{CF}_3\text{OCF}_2\text{CF}_2-$	231.5	270
5	$-(\text{CF}_2)_6-$	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_3\text{CF}_2-$	190	227.5
6	$-(\text{CF}_2)_6-$	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_7\text{CF}_2-$	154	205
7	$-(\text{CFOCF}_2)_3\text{CF}_2(\text{CF}_2\text{OCF})_3-$ <div style="display: flex; justify-content: center; gap: 20px; margin-top: 5px;"> <div style="text-align: center;">  CF<sub>3</sub></div> <div style="text-align: center;">  CF<sub>3</sub></div> </div>	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_7\text{CF}_2-$	182.5	203.5
8	$-(\text{CFOCF}_2)_2\text{CF}_2(\text{CF}_2\text{OCF})_2-$ <div style="display: flex; justify-content: center; gap: 20px; margin-top: 5px;"> <div style="text-align: center;">  CF<sub>3</sub></div> <div style="text-align: center;">  CF<sub>3</sub></div> </div>	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_6\text{CF}_2-$	178	203

From table 3 one may conclude that the available calculation procedure does not allow  $T_c$  forecasting in novel polymer and hence requires updating. Recently Marchionni [12] developed an equation for non-branched perfluoropolyether homo- or co-polymers:

$$T_c = 200 - 80(O/C).$$

The extrapolation of this equation resulted in  $T_c$  equal to 200 K ( $-73^\circ\text{C}$ ) for polytetrafluoroethylene ( $O/C=0$ ), and in  $T_c$  equal to 120 K ( $-153^\circ\text{C}$ ) for homopolymer with structure  $-(\text{CF}_2\text{O})-$ . Below it will be shown that those values differ considerably from our computation results and point to the impossibility of diverging precise functions reasoning only from atomic ratios.

Furthermore A.A. Askadskii proposed a calculation scheme based on the assumption about voluminal dilatation of solid bodies [9,13]. At present such calculation schemes have been developed for quantitative assessment of virtually all polymer properties [14], and the possibility of computer modelling of the synthesis of polymers with designed characteristics has been proved. However, A.A. Askadskii was correct to mention that the applicability of the method decreases as the increments required for calculation accuracy grow in number; and the predictive force of the method may drop to zero, if a novel polymer requires a novel increment to be introduced. Therefore, some polymers e.g., fluoropolymers (never considered by A.A. Askadskii) do not fit in available computational schemes.

We synthesized a series of PFT polymers with different structures of their main and side chains. The analysis of  $T_c$  dependence on the length and structure of their triazine rings cross-linking has shown as follows:

1. The introduction of oxygen into PFT polymer side-chain decreases the impact of the main-chain oxygen on the polymer  $T_c$ ; the said decrease is less obvious for main chains with tetrafluoroethylene oxide links.

2. For polymers with perfluorooxamethylene side-chains only the length of its main-chain influence on the polymer  $T_c$  notwithstanding the presence or absence of oxygen in HFPO links.

3. Starting with  $\text{CF}_3\text{O}(\text{CF}_2\text{O})_2\text{CF}_2-$  radical in side-chain the pattern of  $T_c$  dependence on the length of main-chain changes, and  $T_c$  decreases with the length of polymer main-chain.

Therefore, the effect of oxygen in main-chain differs from that in side-chain, and oxygen in perfluorooxamethylene group inserted into the polymer side-chain provides the maximal effect.

Following [10], our calculation of  $T_c$  in fluoropolymers based on equation (1) with some new increments introduced into it.

Reasoning from the obtained experimental results and taking into account that the contribution of a group does not depend on the nature of adjacent groups only for ideal additivity, and that the best correlation between calculated and experimental results is achieved when group contributions are used instead of those atomic, we made the assumptions as follows:

1. Two  $K_{\text{O}}^X$  increment values must be used in the computational scheme:  $K_{\text{O main}}^X$  for oxygen in the polymer main-chain, and  $K_{\text{O side}}^X$  for oxygen in the polymer side-chain.

2. The minimal  $K_{\text{O}}^X$  value is that of oxygen in perfluorooxamethylene chain.

3. For oxygen surrounded by carbon-containing groups the increment is calculated as the mean of group effects proportional to the number of carbons  $-\text{C}_n-\text{O}-\text{C}_m-$ :

$$K_{\text{O nm}}^X = \frac{K_{\text{O/n}}^X + K_{\text{O/m}}^X}{2} \quad (2)$$

4. An additional increment  $K_{\text{O Tr}}^X$  must be introduced (for triazine ring).

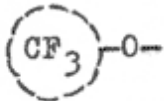

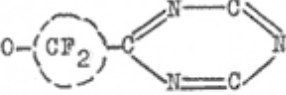

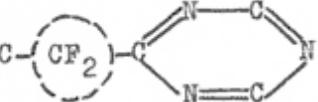

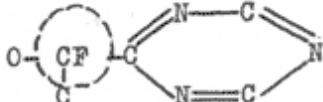
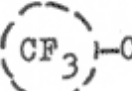


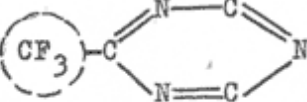
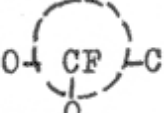


Basing on those assumptions and starting from experimental  $T_c$  in synthesized polymers, and using numerical  $K_i^X$  values published in [6, 10], we solved the redundant equation system based on (1) and determined new  $K_i^X$  values presented in Table 4.

**Table 4.** Numerical values for  $K^X_i$ .

#	Element	Conventional sign	Numerical value ( $\text{cm}^3/\text{mole}$ )
1	Oxygen in side oxamethylene chain	$K^X_{\text{O side}}$	-3.760
2	Oxygen in HFPO links of main chain	$K^X_{\text{O1 main}}$	1.324
3	Oxygen in TFEO links of main chain	$K^X_{\text{O2 main}}$	-1.220
4	Triazine ring	$K^X_{\text{Tr}}$	32.077

Van der Waals volume for a chain link is calculated as a sum of volume increments  $\Delta V_i$  shown in Table 5 and taken from published data [10, 15].

**Table 5.** Increments for van der Waals atomic group volume.

#	Group of atoms	$\Delta V_i \cdot 10^{24} (\text{cm}^3)$
1		41.9
2		3.4
3		30.3
4		54.7
5		27.3
6		27.5
7		19.0
8		38.8
9		30.65
10		19.3
11		38.5
12		22.3
13		17.1
14		33.7*

\* Calculated by us

Those newly determined increments we used to calculate  $T_c$  in synthesized PTF polymers. A comparison between calculated and experimental values shows that both positive and negative deviations and their maximal values are virtually the same (mean square deviation was  $\pm 3.1$  K), thus confirming the correctness and validity of the calculation scheme.

Figure 1 shows the calculated dependence of  $T_c$  on

$\sum_i \left( K_i^x / N_A \right) \cdot \sum_i \Delta V_i$ , that is essentially fits all experimental data.

However, there are some points that poorly fit the calculated curve. They belong to polymers with long perfluoroalkyl side chains. Their deviations of experimental  $T_C$  from those calculated with the proposed technique were negative and the quadratic mean deviation was  $-12.5$ . For those structures the nature of increments must be revised. It is obvious that in those polymers the impact of their main-chain carbons on  $T_C$  differs from that of side-chain carbons.

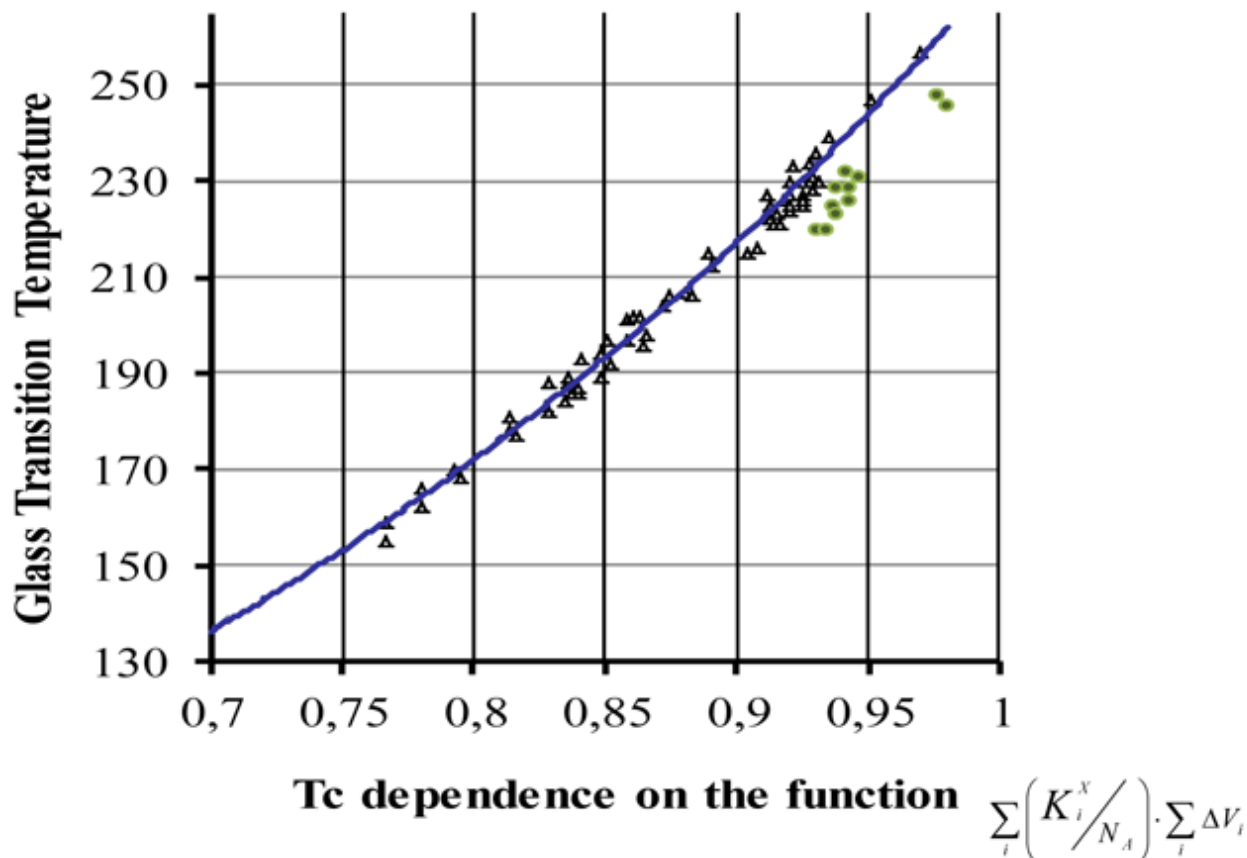


Fig. 1.

To check our earlier assumptions we calculated  $T_C$  in some perfluoropolyethers, and the results are present in Table 6.

Table 6. Calculated and experimental  $T_C$  in perfluoropolyethers.

#	Polyether	$T_C$ (K) experimental	$T_C$ (K)* calculated	Reference
1	$-\left[ (\text{CF}_2\text{CF}_2\text{O})_p (\text{CF}_2\text{O})_q \right]_n -$ p/q = 0.6, 0.7	142	136.5	[16]
2	$-(\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O})_n -$ $-(\text{CFCF}_2\text{O})_n -$	208	221	[17]
4	$\text{CF}_3$	201	204.5	NIISK
5	$-(\text{CF}_2\text{O})_n -$	-	102.5	-

\*  $T_c$  calculation in polymers with trifluoromethyl side-groups are carried out with  $K_{O_2 \text{ main}}^X$  increment, while in polymers without side-chains with  $K_{O \text{ side}}^X$ .

From table 6 one may see that the convergency of experimental and calculated results is not very high, and its mean square deviation is  $\pm 7.7$ . However, taking into account that the method for  $T_c$  determination differed from that used by us, and that those polymers are mostly low-molecular, this deviation may be considered as satisfactory. Therefore, we estimated the limit  $T_c$  in polyethers, its calculated value in polydifluoromethylene oxide is  $-170.5^\circ\text{C}$ .

The proposed method for the calculation of glass transition temperature was applied as well in the calculation of  $T_c$  of carbochain co-polymers of perfluoroalkylvinyl ethers and vinylidene fluoride  $[(\text{CH}_2\text{CF}_2)_3\text{CF}(\text{R}_f)\text{CF}_2]_n$  manufactured in our institute by the emulsion polymerization. For them the deviation of calculated values from those determined experimentally was somewhat higher than for perfluoroalkyltetrazine:  $\pm 5.8 \text{ K}$ .

**Table 7.** Structures,  $T_c$ ,  $\lg T_c$  and  $\sum_i K_{O_{\text{side}}(nm)i}^X / K_{O_{\text{side}}}^X$  copolymers of vinylidene fluoride and perfluorovinyl ethers  $-(\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{CH}_2\text{CF}_2\text{CF}(\text{R}_f)\text{CF}_2)_n-$

#	Rf	$T_c$ (K) [11]	$\lg T_c$	$\sum_i K_{O_{\text{side}}(nm)i}^X / K_{O_{\text{side}}}^X$
1	$\text{CF}_3\text{O}-$	233	2.367	0.50
2	$\text{CF}_3\text{CF}_2\text{O}-$	246	2.391	0.25
3	$\text{CF}_3\text{CF}_2\text{CF}_2\text{O}-$	240	2.380	0.17
4	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2\text{O}-$	241	2.382	0.12
5	$\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{O}-$	223	2.348	0.83
6	$\text{CF}_3\text{OCF}_2\text{CF}_2\text{O}-$	232	2.365	1.00
7	$\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_2-$	213	2.328	1.50
8	$\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_3-$	203	2.307	2.00
9	$\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_4-$	194	2.288	2.50
10	$\text{CF}_3\text{CF}_2\text{OCF}_2\text{CF}_2\text{O}-$	230	2.362	0.75
11	$\text{CF}_3\text{OCF}_2\text{OCF}_2\text{CF}_2\text{O}-$	208	2.318	2.00
12	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_2\text{CF}_2\text{CF}_2\text{O}-$	199	2.299	3.00
13	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_3\text{CF}_2\text{CF}_2\text{O}-$	178	2.250	4.00
14	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_4\text{CF}_2\text{CF}_2\text{O}-$	161	2.207	5.00
15	$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{O}-$	235	2.371	0.50
16	$\text{CF}_3\text{OCF}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{O}-$	218	2.338	1.17

On the basis of table 7 were derived the dependence of  $\lg T_c$  on  $\sum_i K_{O_{\text{side}}(nm)i}^X / K_{O_{\text{side}}}^X$ , expressed by the following equation:



$$\lg T_C = 2.390 - 0.0346 \cdot \sum_i K_{O_{side}(nm)i}^X / K_{O_{side}}^X \quad (3)$$

or in less complicated form:

$$\lg T_C = 2.390 - 0.0346 \cdot \sum \frac{1/n_i + 1/m_i}{2} \quad (4)$$

This dependence makes it possible to forecast  $T_C$  in polymers with the above-mentioned compositions with any perfluorovinyl ether. Similar equations may be derived for any comb-shaped polymers with perfluorooxaalkyl side-chains. E.g., for polymers  $-(CF_2CF(R_f)O)_4CF_2O)_n-$

$$\lg T_C = 2.226 - 0.0047 \cdot \sum \frac{1/n_i + 1/m_i}{2} \quad (5)$$

For polymers with general formula  $-[PN(OCH_2R_f)_2]_n-$

$$\lg T_C = 2.250 - 0.014 \cdot \sum \frac{1/n_i + 1/m_i}{2} \quad (6),$$

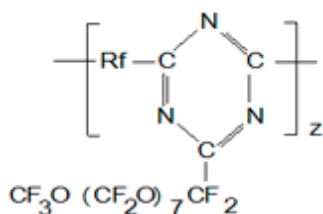
It fits very well experimental data (mean square deviation does not exceed  $\pm 2$ ). The general equation for comb-shaped polymers with perfluorooxaalkyl side-chains is as follows:

$$\lg T_C = A + B \cdot \sum \frac{1/n_i + 1/m_i}{2}, \quad (7)$$

Here A and B are constants for this polymer series. Those equations allow sufficient accuracy in the forecasting of  $T_C$  in such polymers and rule out complicated calculations using the above algorithm.

As it was already mentioned we have studied experimentally the dependence of  $T_C$  in PTF polymers with perfluorooxamethylene side chains on the length of their main chain that contained oxygen in the form of HFPO links, or containing no oxygen. Those were straight-line functions with  $T_C$  decreasing with the main chain length. It was interesting to study similar functions for polymers with oxygens in TFEO included into their main chains. Being not able to synthesize such polymers currently we calculated their  $T_C$  using the refined calculation scheme. The results are shown in Table 8.

**Table 8.** Calculated  $T_C$  in polymers.



#       $R_f$        $T_C$  (K) calculated

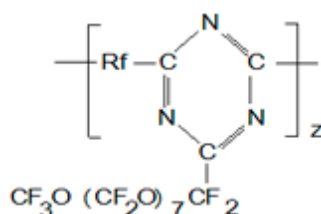
- 1  $-(CF_2OCF_2)_2-$  139.5
- 2  $-(CF_2OCF_2)_3-$  143.5
- 3  $-(CF_2OCF_2)_4-$  147
- 4  $-(CF_2OCF_2)_5-$  149.5
- 5  $-(CF_2OCF_2)_6-$  152

- 6 –(CF2OCF2)7– 154  
 7 –(CF2OCF2)8– 156  
 8 –(CF2OCF2)9– 157.5

From Table 8 one may see for the polymers with TFEO-oxygens the same inverse relationship between the main chain length and  $T_c$ , and as the main chain length increases  $T_c$  tend to a constant value. It should be noted that for those polymers their  $T_c$  is 15-30K lower than those of similar polymers containing oxygens in OHFP-links of their main chains. It must be due to large contribution of TFEO-link oxygens into the total chain flexibility.

When going from HFPO-linked oxygen to TFEO-linked oxygen  $K_{O\text{ main}}^X$  values change from positive to negative and approach  $K_{O\text{ side}}^X$  of perfluorooxamethylene links, i.e. the main chain becomes less flexible and less different from the side-chain. Taking it into account and having in mind  $T_c$  calculated for perfluoropolyethers (Table 6) one may assume that in the case of perfluorooxamethylene main chain its  $K_{O3\text{ main}}^X$  is equal to  $K_{O\text{ side}}^X$  for perfluorooxamethylene side-chain, i.e  $K_{O3\text{ main}}^X$  is  $-3.76$ . The difference between  $K_{O2\text{ main}}^X$  and  $K_{O1\text{ main}}^X$ , is equal to that between  $K_{O3\text{ main}}^X$  and  $K_{O2\text{ main}}^X$ , thus confirming to some extent our above assumptions. Reasoning from it we calculated  $T_c$  in polymers with perfluorooxamethylene links in their main and side-chains (table 9).

**Table 9.** Calculated  $T_c$  in polymers.



#	$R_f$	$T_c$ (K) calculated
1	–CF2OCF2OCF2–	132
2	–CF2O(CF2O)2CF2–	129.5
3	–CF2O(CF2O)3CF2–	127.5
4	–CF2O(CF2O)4CF2–	126
5	–CF2O(CF2O)5CF2–	124.5
6	–CF2O(CF2O)6CF2–	123
7	–CF2O(CF2O)7CF2–	122

From table 9 one may see that in this case the dependence of  $T_c$  on the main chain length, i.e. as the main chain length increases  $T_c$  decreases and tends to a constant value. Obviously, the minimal  $T_c$  possible in polymers with above mentioned structures must be about 123 K ( $-150^\circ\text{C}$ ).

We used thus developed calculation scheme to determine  $T_c$  in a number of oxygen-containing fluoropolymers, mostly not synthesized yet. Those polymers' structures and  $T_c$  are shown in table 10.

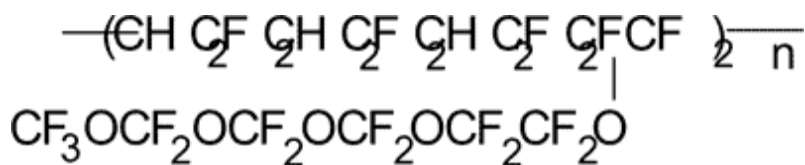
**Table 10. Calculated and experimental  $T_c$  in oxygen-containing fluoropolymers**

From table 10 one may see that the drop of  $T_c$  in polymers with long perfluorooxamethylene side-chains is more prominent in polymers with rigid main chain (perfluorocarbons). Similar behaviour was observed in comb-shaped polymers with  $-\text{CH}_2-$  links in their side-chains [1]. It should be mentioned as well that polymers with flexible main chains and long perfluorooxamethylene side-chains have nearly the same  $T_c$  that and as the number of  $-\text{CF}_2\text{O}-$  links increases their  $T_c$  tends to  $T_c$  of polyperfluorooxamethylene, that is 102.5 K ( $-170.5^\circ\text{C}$ ). The same trend is valid for other polymers but evening-out of their  $T_c$  occurs at higher content of  $-\text{CF}_2\text{O}-$  links. Therefore, one may suggest that for any comb-shaped polymers with perfluorooxamethylene links in their side-chains  $T_c$  is not less than 102.5K ( $-170.5^\circ\text{C}$ ) that is the minimal  $T_c$  value for fluoropolymers.

### Examples of vitrification temperature calculation in fluoropolymers



Calculation of  $T_c$  in polymer with the structure as follows:



$$\sum_i \Delta V_i = 3 \cdot 33.7 + 3 \cdot 17.1 + 41.9 + 5 \cdot 3.4 + 4 \cdot 27.5 + 2 \cdot 30.65 + 19.3 = 401.9 \cdot 10^{-24} \text{ cm}^3$$

$$N_A \cdot \sum_i \Delta V_i = 242.064 \text{ cm}^3 / \text{mole}$$

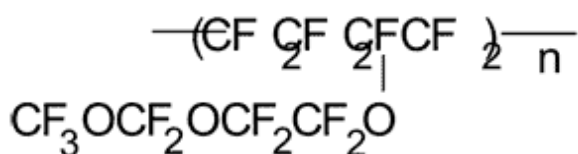
$$\begin{aligned} \sum_i K_i^X &= 14 \cdot K_C^X + 22 \cdot K_F^X + 6 \cdot K_H^X + 3 \cdot K_{O_{side}}^X + \frac{K_{O_{side}}^X / 2 + K_{O_{side}}^X}{2} + \frac{K_{O_{side}}^X}{4} + \frac{K_h^X}{2} = \\ &= 14 \cdot 10.739 + 22 \cdot 2.944 - 7.488 - 11.28 - 2.82 - 0.94 + 3.669 = 196.255 \text{ cm}^3 / \text{mole} \end{aligned}$$

$$\lg T_c = 2.2458$$

$$T_c = 176 \text{ K}$$

$K_{O}^X$  for oxygen adjacent to the main chain is taken to be equal to  $\frac{1}{2}$  of  $K_{O}^X$  for oxygen surrounded of another adjacent group. For copolymers with similar structures it is  $\frac{1}{2}K_h^X$ .

Calculation of  $T_c$  in polymer with the structure as follows:



$$\sum_i \Delta V_i = 41.9 + 3 \cdot 3.4 + 3 \cdot 27.5 + 2 \cdot 30.65 + 33.7 + 19.3 = 248.9 \cdot 10^{-24} \text{ cm}^3$$

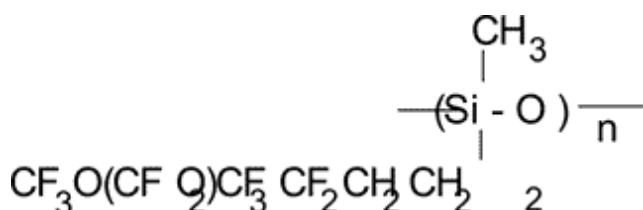
$$N_A \cdot \sum_i \Delta V_i = 149.9125 \text{ cm}^3 / \text{mole}$$

$$\begin{aligned} \sum_i K_i^X &= 8 \cdot K_C^X + 16 \cdot K_F^X + \frac{1}{2} \cdot K_d^X + K_{O_{side}}^X + \frac{K_{O_{side}}^X / 2 + K_{O_{side}}^X}{2} + \frac{K_{O_{side}}^X}{4} = \\ &= 8 \cdot 10.739 + 16 \cdot 2.944 + \frac{1}{2} \cdot 7.827 - 3.76 + \frac{-3.76 / 2 - 3.76}{2} - \frac{3.76}{4} = 129.409 \text{ cm}^3 / \text{mole} \end{aligned}$$

$$T_c = 198,5 \text{ K}$$

For those copolymers we take  $\frac{1}{2}K_d^X$ .

Calculation of  $T_c$  in polymer with the structure as follows:



In order to calculate  $T_c$  in such polymers we calculated  $V_i$  for  $\text{C}-\text{CH}_2\text{Si}$  group  $16.0 \cdot 10^{-24} \text{ cm}^3$ . The numerical  $K_{O}^X$  value for oxygen connected to two silicons  $K_{O_{Si}}^X$  was calculated from the experimental

data on  $T_C$  in polymers that was equal to  $-7.02 \text{ cm}^3/\text{mole}$ .

$$\sum \Delta V_i = 41.9 + 4 \cdot 3.4 + 3 \cdot 33.7 + 30.65 + 27.5 + 17.1 + 16.0 + 22.0 + 27.6 + 0.49 = 297.94 \cdot 10^{-24} \text{ cm}^3$$
$$N_A \cdot \sum \Delta V_i = 179.449 \text{ cm}^3 / \text{mole}$$

$$\sum_i K_i^X = 9 \cdot K_C^X + 13 \cdot K_F^X + 7 \cdot K_H^X + 3 \cdot K_{O_{side}}^X + K_{O_{side}}^X / 2 + K_{Si}^X + K_{OSi}^X =$$
$$= 9 \cdot 10.739 + 13 \cdot 2.944 + 7 \cdot 1.248 - 3 \cdot 3.76 - 1.88 + 19.570 - 7.02 = 125.577 \text{ cm}^3 / \text{mole}$$

$$\lg T_C = 2.1348$$

$$T_C = 136.4 \text{ K}$$

Therefore, basing on the investigation of the impact of ether bond located in the side- or main chain of PFT polymers on their  $T_C$  we have further developed the algorithm earlier proposed by Askadskii and Slonimsky for the computational forecasting of glass transitional temperatures in fluoropolymers and proved its applicability for a large series of polymer structures. Those calculations have shown the principal possibility of synthesis of triazine polymers with perfluorooxamethylene structures in all its fragments with  $T_C$  up to 123 K ( $-150^\circ\text{C}$ ) and the synthesis of polyperfluorooxamethylene with  $T_C$  equal to 102.5 K ( $-170.5^\circ\text{C}$ ). The minimal achievable  $T_C$  in any fluoropolymer is 102.5 K. An empiric equation is proposed for the forecasting of  $T_C$  in any comb-shaped polymers with perfluorooxaalkyl side-chains, and its applicability is shown.

The results obtained with the help of the developed calculation scheme made it possible to produce perfluorotriazine liquids with wide temperature range of applicability [18-21]. Those liquids are used for the base in plastic lubricants and antioxidant-anticorrosion additives to perfluoropolyethers and plastic lubricants based on them.

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