Use of perfluoroacylfluorides for the synthesis of perfluoroalkylvinyl ethers. Part III.

Dependence of frost-resistance of fluoropolymers on the structure of vinyl ethers of general formula $CF_3O(CF_2CF_2O)mCF{=}CF_2$ and $CF_3O(CF_2O)nCF_2CF_2OCF{=}CF_2$

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At present an increase in frost-resistance have been remained one of primary tasks of fluoropolymer chemistry [1,2]. Introduction of oxygen atoms into fluoropolymers allow to reduce significantly the glass transition temperature of these thermally stable and chemically inert compounds [3-5].

The oxygen introduction into the main chain of fluoropolymers is known to obtain perfluoropolyether oils able to work under cryogenic conditions. Good low-temperature properties of such polymers are explained by weak intermolecular interaction and an increase in mobility of individual chain links of macromolecules due to a low energy barrier of rotation around the −CF_2-O- bonds [3].

The glass-transition temperature of a polymer is also influenced by the size, polarity and mobility of side groups [2,6]. In this connection, perfluorinated vinyl ethers take on special significance because their copolymerization with other fluoroolefins may result in high-molecular , able to be vulcanized copolymers with oxygen-containing side groups of different length.

As a result of investigations, samples of copolymers with vinylidene fluoride with a glass-transition temperature to −105^{o}C were produced on the basis of synthesized vinyl ethers (VE) of general formula $CF_3O(CF_2CF_2O)_mCF{=}CF_2$ (I) [7] and $CF_3O(CF_2O)_nCF_2CF_2OCF{=}CF_2$ (II) [8] .

Copolymers of vinylidene fluoride with VE I and II differ in the length of side chains and in the ratio of oxygen and carbon atoms in these chains. In copolymers C-II of the general formula

$$\left[\begin{array}{l} —(CF_2\text{-}CH_2)_3—(CF_2\text{-}CF)_1— \\ \quad CF_3O(CF_2O)_nCF_2CF_2O \end{array}\right]_l,$$

obtained on the basis of VE II, abundance of the oxygen atoms in the side chains at the equal length of these chains is always greater than in copolymers C-I of the general formula

$$\left[\begin{array}{l} -(CF_2\text{-}CH_2)_3-(CF_2\text{-}CF)_1- \\ \qquad\qquad\quad CF_3O(CF_2CF_2O)_m \end{array}\right]_1,$$

obtained on the basis of VE I. Moreover, the growth of the length of the side chains of copolymer C-II is followed by an increase in the ratio of oxygen/carbon while the growth of the length of the side chains of copolymer C-! is followed by a decrease (though not very significant) of this ratio (table and Fig.1)

Table. *Dependence of the glass transition temperatures of copolymers C-I and C-II on the length of the side chains and on the ratio of oxygen/carbon*

I			II		
P**	O/C	$T_{g\text{-}t}$ ^oC	P**	O/C	$T_{g\text{-}t}$ ^oC
5	0.67	-41	7	0.75	-65
8	0.60	-55 /-60	9	0.80	-70/-71
11	0.57	-70/-72	11	0.83	-90
14	0.56	-76/-79	13	0.86	-105

P** is the total number of oxygen and carbon atoms in the side chains.

The table and Figure show total influence of the two factors: the length of the side chains and the ratio of oxygen/carbon atoms on the glass-transition temperature of the copolymers.

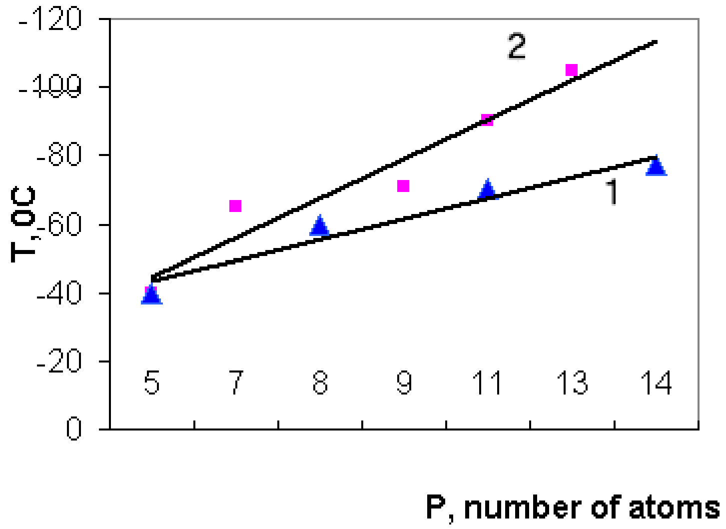

Fig.1 *Dependence of the glass-transition temperature of copolymers C-I and C-II on the length of the side chains.*

P is the total number of oxygen and carbon atoms in the side chains of the copolymers: 1-copolymer C-I; 2-copolymer C-II.

The results presented in the table and figure show that the growth of the length of the side chains leads to the decrease in the glass-transition temperature of the copolymers produced, and a more drastic decrease in the glass-transition temperature is typical of the polymers containing difluoromethyleneoxide chain links according to the great value of the ratio of oxygen/carbon atoms in them.

When the P value is about 14, the glass -transition temperature of the copolymer containing tetrafluoroethyleneoxide groups is close to the minimal possible one while a further increase in the length of the side chains containing difluoromethylene oxide links may result in a decrease in the glass-transition temperature of the copolymers. Nevertheless, copolymers C-I should find application at temperatures above -80^{o}C obviously the same as copolymers C-II because tetrafluoroethylene, which is a raw material for the synthesis of VE I, is the most available and cheapest fluoroolefin.

Thus, the synthesis of two series I and II of perfluoroalkylvinyl ethers has allowed to evaluate combined influence of the length of the side chains and abundance of the oxygen atoms in these chains on the glass-transition temperature of the copolymers with vinylidene fluoride.

References

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