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Telomeres of Tetrafluoroethylene - Advanced Materials to Create Superhydrophobic Coatings and Optical Fiber with Low Attenuation Coefficient

A.F. Shestakov

Institute of Problems of Chemical Phisics RAS, Academician Semenov Avenue 1, Chernogolovka, Moscow region, Russian Federation

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The paper describes formation of telomers of tetrafluoroethylene (TFE), which are very interesting intermediate materials of different purposes, by radiation polymerization. In some cases there are formed long chained oligomers suitable for creation of superhydrophobic coatings. In such systems formation of gels is observed under low TFE content. Quantum chemical analysis allows to reveal the factors that are responsible for this phenomenon. In the case of solvents with appropriate cyclic structure, short chain oligomers, which have low C-H bonds content, are raw materials for fluoropolymers suitable for manufacturing optical fibers. The work is aimed to predict which types of materials are formed under polymerization conditions. For these purposes the generalized Polany-Semenov rule is used. Its parameters found by DFT calculations can be recommended for practical applications in the molecular design of new fluorine-containing polymers.

Keywords: Tetrafluoroethylene, Telomerization, DFT Calculation, Activation Energy, Superhydrophobic Coating.

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1. INTRODUCTION

Recently, much attention is paid to the creation of superhydrophobic coatings on the basis of the effect of the surface of the lotus flower, which have numerous applications. Formation of very grainy surfaces, which consist of regularly arranged micro needles of the same height in the limit, always gives a hydrophobic effect. However, under use of hydrophobic materials, this effect is further enhanced.

Another promising direction is decreasing content of C-H bonds in the polymeric material of optical fiber, which are the main cause for attenuation of the light beam. If the value of attenuation coefficient of such fibers will be reduced it may result in "revolution" in the optical transmission.

Fluorinated telomers are very promising materials for these areas as they are hydrophobic and have a low content of C-H bonds with high stretching vibrations. Direct use for these purposes of Teflon, the product of tetrafluoroethylene (TFE) polymerization is difficult because of its insolubility in practice in all known solvents, as well as due considerable difficulties in its conversion into a suspension of microparticles. In this situation, TFE oligomers are very interesting as intermediate materials. They are obtained by radiation polymerization in a suitable solvent.

$$RH \xrightarrow{h\upsilon} R^{\bullet} \tag{1.1}$$

$$R^{\bullet} + n\, C_2F_4 \rightarrow R(C_2F_4)_n^{\bullet} \tag{1.2}$$

$$R(C_2F_4)_n^{\bullet} + RH \rightarrow R(C_2F_4)_nH + R^{\bullet} \tag{1.3}$$

Depending on the degree of polymerization n TFE oligomers obtained have various purposes. Telomeres with n ~ 10-20 are promising for the development of coatings. When n is low and a solvent has suitable molecular structure the compounds obtained are raw materials for fluoropolymers suitable for manufacturing optical fibers.

2. EXPERIMENTAL

At slow chain transfer to a solvent (step 1.3), in particular when acetone is used as the solvent, gels are obtained under very low content of TFE, about 0.3 M [1]. Dense gels contain at least four molecules of solvent per unit of TFE. The use of quantum-chemical and spectroscopic methods [2-3] made it possible to find out what this surprising phenomenon is due to two reasons. First, due to the formation of weak hydrogen bonds between the molecules of the solvent and oligomer supramolecular structures arise. They have the shell of one layer of acetone molecules around the polymer chain $(C_2F_4)_n$ (see Figure 1 a).

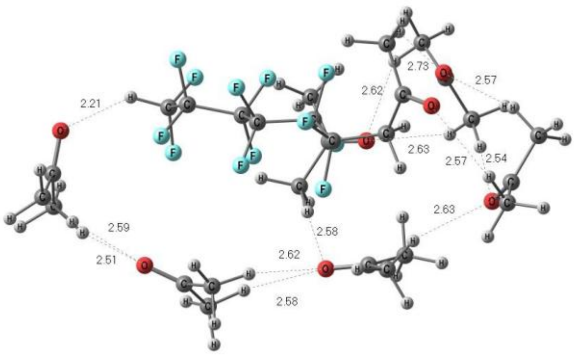
Calculations [2] show that the energy gain at acetone molecules entering in the solvation "coat" of telomere from liquid acetone is about 2 kcal/mol. By combining the solvation shells of neighboring telomeres (see Figure 1 b), this leads to an effective increase in the volume per one molecule telomere. And secondly, due to the formation of stronger hydrogen bonds ~ 4 kcal/mol between the end CF_2H group and the carbonyl group of the residue of an acetone molecule associated with another oligomer (see Figure 1 c). As the result, some oligomer molecules forms a longer supramolecular complex. This promotes the formation of a grid at low concentrations of TFE.

Under heat treatment of the gel of telomere solvent evaporates, and a strong coating is formed due to an adhesion of the fluorocarbon residues. They have a typical surface roughness of 320 nm [4] due to the formation of particles with a block size of 100-1500 nm.

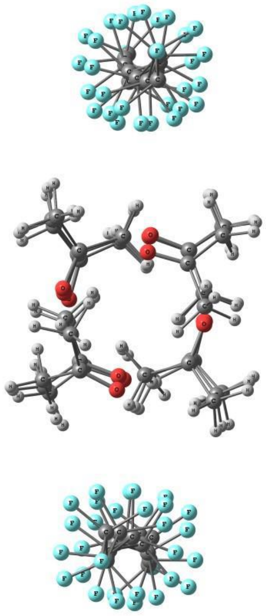
By using the properties of the gel when it is applied to a surface one can enhance the degree of roughness of the surface by forming a lotus type structure to create super hydrophobic coatings.

At higher temperatures, reactions of chemical cross-linking are also possible [4]. They lead to elongation of the length of the macromolecular chains.

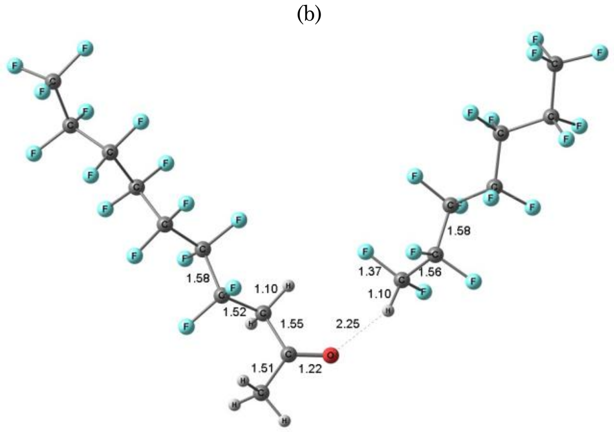
$$R(C_2F_4)_nH + R(C_2F_4)_mH \rightarrow R(C_2F_4)_{n+m}H + RH \quad (2.1)$$



(a)



(b)



(c)

Fig. 1. The structure of the complexes $H(C_2F_4)_3CH_2COCH_3$ * $(CH_3COCH_3)_6$ (a), $F(C_2F_4)_7F$ $(CH_3COCH_3)_{12}$ $F(C_2F_4)_7F$ (b) and $C_6F_{13}CF_2H$* $CH_3COCH_2C_7F_{15}$ (c). The bond lengths are in Å.

When using THF as solvent short chain oligomers were obtained $n \leq 3$ [5]. As it is known, there are methods of THF polymerization, therefore from molecules of THF with fluorocarbon substituents branched fluorine-containing polymers can be prepared. They have a flexible backbone with polar ether groups and side fluorocarbon substituents, making such polymeric materials promising for the manufacture of optical fiber. Due to low content of C-H bonds in it, the damping rate at the propagation of light pulses is reduced.

3. RESULTS AND DISCUSSION

Thus, to develop novel fluorinated monomers the problem arises how to predict their composition (n) for a selected solvent. To solve it, it has been developed an approach based on the use of the generalized Polanyi-Semenov rule. In result, [6] the relationship between activation energy E_a of the key step (1.3) of the chain transfer and the enthalpy of reaction (1.3) ΔH was obtained

$$E_a = A + \Delta H/2 + (\Delta H)^2/(2W) \quad (3.1)$$

The ΔH value is linearly related to the enthalpy of R-H bond cleavage in the solvent molecule $\Delta H = \Delta H_{R\text{-}H} - 98.9$ kcal/mol.

Theoretical studies carried out for a wide variety of solvents of different types: alcohols, ketones, esters and ethers show that the chain termination reaction can be divided into 2 classes. The first class includes the reaction of H atom abstraction from the α-CH bonds of alcohols and ethers, aliphatic and cyclic. In this case, the activation energy of thermoneutral reaction A is equal to 4.3 kcal/mol and the energetic coefficient W = 40 kcal/mol. For the rest cases, A = 8.45 kcal/mol, W = 42.8 kcal/mol. Using these parameters, the calculated activation energies are described with an error less than 1 kcal/mol. The results of these calculations are consistent with the available experimental data on the formation of short-chain oligomers in the case of low values of the activation energies (when the chain transfer processes are effectively compete with the processes of macroradical growth) and long-chain oligomers at higher values. Thus, the generalized Polany-Semenov relationship (3.1) with the parameters found can be recommended for practical applications in the molecular design of new fluorine-containing polymers.

As an example, Fig. 2 shows the calculated structure of the branched polymer from the telomere with n = 2, based on propylene oxide.

4. CONCLUSIONS

For example of acetone molecules intermolecular interaction between solvent and tfe oligomers were analyzed using quantum chemical methods. Multiple solvent-solvent and solvent-telomer hydrogen bonds lead to the spatially correlated arrangement of telomers and to the formation of a network, which determines the internal structure of both colloid particles and the gel into which the colloid particles transform with an increase in the network density. It was carried out the theoretical study of the key step of the chain transfer to a molecule of solvent of different types: alcohols, ketones, esters and ethers. Using of the generalized Polany-Semenov relationship allows to find regularities, which governs the chain length of the oligomers formed in such systems. They can be recommended for practical applications in the molecular design of new fluorine-containing polymers.

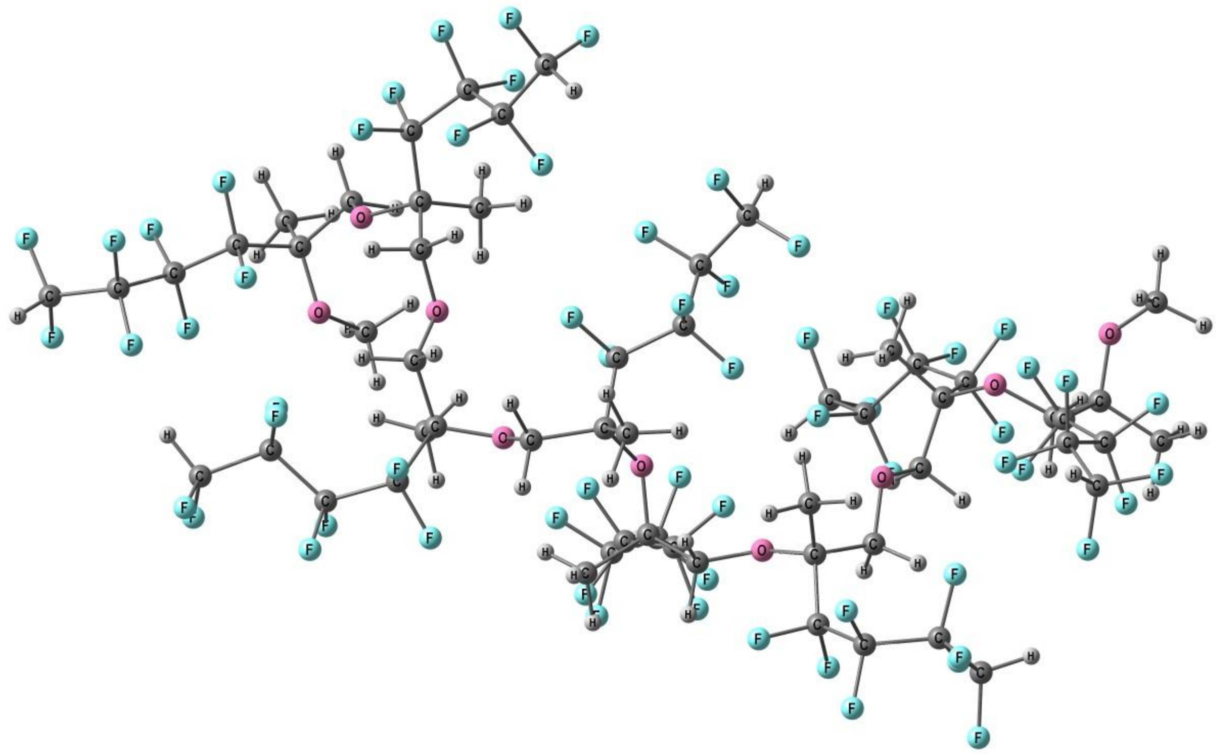


Fig. 2 – The optimized structure of the fragment $CH_3O(CH_2C(CH_3)(C_4F_8H))_8OCH_3$ $OCH_3)_6$ of branched fluoropolymer according to the PBE / SBK calculation.

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