STRUCTURE OF IRRADIATED POLYTETRAFLUOROETHYLENE ACCORDING TO DFT
CALCULATIONS OF NMR CHEMICAL SHIFTS

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Methods of density functional theory were used to calculate 1H, 13C, and 19F magnetic shielding tensors for C7F_nH_mO_l model molecules, which can arise as fragments from radiation exposure of polytetrafluoroethylene.

Keywords: polytetrafluoroethylene, radiation exposure, NMR chemical shift, quantum chemical computations.

As is known, irradiation of polytetrafluoroethylene gives rise to additional 19F NMR signals [1, 2]. They are supposed to be due to the formation of trifluoromethyl groups, incorporation of oxygen and hydrogen atoms in the fluoroethylene chains, elimination of fluorine atoms, and other processes. The diversity of variants hinders identification and interpretation of experimental data.

To elucidate the nature of the observed microscopic structural changes of polytetrafluoroethylene (PTFE) after electronic irradiation, we performed DFT quantum chemical calculations of the 19F, 1H, and 13C NMR chemical shifts for modified models of oligomer chains with different arrangements of oxygen and hydrogen atoms and CF_n groups.

DETAILS OF COMPUTATION

For molecular structure calculations, we used the ADF program complex [3] in which the optimization procedure [4] for local-exchange correlations involved the functional from [5]. Gradient corrections were applied by the procedure of [6]. The polarized triple-zeta Slater orbitals without a core potential [3] were used as atomic wave functions for H, C, and F atoms. The initial molecular structure of C7F_nH_mO_l was set in the form of a flat zigzag of carbon atoms (and substitution atoms). Geometry optimization of the calculated fragments was performed without any restrictions on molecular symmetry (extremely low C1 point symmetry). The parameters of the 1H, 13C, and 19F magnetic shielding tensors were calculated with the ADF program complex [3] using the procedure of [7-9]. Exchange correlations were approximated with BLYP functionals [10, 11]. The wave functions for H, C, and F atoms were chosen the same as in the optimization procedure. Successful computations of NMR chemical shifts for similar molecular fragments was demonstrated by computations and correlation with experiment in ultradisperse polytetrafluoroethylene [12].


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RESULTS AND DISCUSSION

Experimental data on $^{19}$F NMR chemical shifts are available for the initial sample (commercial PTFE product) and irradiated samples [1, 2] (Figs. 1 and 2). According to these data, the initial PTFE sample is characterized by an intense $^{19}$F signal from CF$_2$ groups, which are elements comprising the polymer macromolecule; the shift of the signal is $\delta_{CF_2} = -122$ ppm relative to the signal of the CFCl$_3$ standard. Irradiation of a PTFE sample with an electron beam with an energy of 1 MeV and irradiation dose of 4 MGy was supposed [1,2] to give rise to new CF$_2$ groups with $\delta_{CF_2} = -126$ ppm. In addition, it was assumed that a CF group with $\delta_{CF} = -185$ ppm appears along with CF$_3$ groups with $\delta_{CF_3} = -83$ ppm and $-70$ ppm and that irradiation in air and oxygen leads to O–CF$_2$ with $\delta_{CF_2} = -90$ ppm. The following model systems were used for theoretical studies: C$_7$F$_{14}$ (with a terminal CF$_2$ group: CF$_2$=CF–CF$_2$ and one terminal CF$_3$ group, see Fig. 1), C$_7$F$_{14}$O (with an oxygen atom double-bonded to C in the middle of the chain and two CF$_3$ terminal groups, see Fig. 2a), C$_6$F$_{14}$O (with a terminal oxygen atom and one terminal CF$_3$ group, see Fig. 2b), C$_7$F$_{14}$H$_6$ (with two terminal CF$_3$ groups and alternating CF$_2$ and CH$_2$ units, Fig. 3), C$_7$F$_{18}$ (with three CF$_3$ groups, two of which are terminal and one is in the middle of the chain, Fig. 4).

The average values of the parameters of chemical bonds for the model systems obtained by optimization are given in Table 1 in comparison with the experimental values of interatomic distances. The results indicate that there is good...