The Nature of Color Centers in γ-Irradiated Poly(tetrafluoroethylene)


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Received May 8, 2007; Revised Manuscript Received November 9, 2007

Abstract—The quantum-chemical investigation of tentative products of radiation-chemical transformations in PTFE under the action of γ radiation at a temperature higher than the melting point of the crystalline phase has been carried out. The excited electronic states of fluorinated alkylpolyenes of the general formula \(\text{F}_{3}\text{C}-(\text{CF}=\text{CF})_n\text{CF}_3\) \((n = 1–7)\), the same compounds with CFO terminal groups, and the dimers of monomer fragments containing two or more conjugated double bonds have been calculated by means of the semiempirical PM3 method. In addition, the excited states for PTFE chain fragments of different lengths have been calculated. On the basis of calculations, it has been concluded that the coloration of the irradiated PTFE may be caused by formation of polyconjugated structures in the polymer chain with the number of double bonds \(n = 2–6\).

DOI: 10.1134/S1560090408050035

Over the last years, increased attention has been paid to radiation-chemical processes that proceed in PTFE at temperatures above the melting point of the crystalline phase (327°С) [1–4]. It was found that irradiation of the polymer in the melt brings about improvement of its valuable properties (the elastic modulus, the yield point, and the radiation resistance). The IR and NMR studies allowed one to determine the character of chemical transformations in a polymeric matrix under irradiation. The experimental data showed that the chain branches –CF\(_2\), side branches >CF–CF\(_3\) and >CF–CF\(_2\), terminal groups –CFO and –CF\(_3\), and double bonds –FC=CF– and –CF=CF\(_2\) form in the irradiated PTFE [1–4].

In [5], the chemical transformations of the irradiated PTFE melt were investigated by fluorescence techniques. PTFE films subjected to γ irradiation at a temperature near the melting point under vacuum or argon acquired fluorescent behavior and color. The samples irradiated under argon (the dose was 0.2 MGy) with a minor content of air oxygen (~10\(^{-4}\) mmHg) were distinguished by the brightest fluorescence. The fluorescent properties and color were assumed to be associated with the color centers of different types, whose concentration ratio depended on irradiation conditions. It was hypothesized that the fluorescent centers originated under the radiation modification of the PTFE melt are polyene structures with different numbers of conjugated double bonds. Alkylpolyenes of the general formula \(\text{H}_n\text{C}-(\text{CH}=\text{CH})_n\text{CH}_3\) may serve as suitable model compounds for these conjugated structures. A comparison of the absorption spectra of the models under consideration and the positions of the band maxima in the fluorescence excitation spectra of the irradiated PTFE made it possible to infer that the samples under study contain polyconjugated fragments carrying from 4 to 11 double bonds [5].

The goal of this study was to perform the quantum-chemical investigation of tentative products arising in the radiation-chemical transformation of PTFE.

THEORY

The Geometrical Model

The precise geometry of the studied compounds is unknown. Therefore, initial computations were performed by the methods of molecular dynamics for optimization of the equilibrium structure of molecules in the ground electronic state. In all geometry variants, the minimum energy in the ground electronic state corresponds to structures where the fragment with conjugated bonds has an almost planar structure. The alkyl fragment deviates from this plane; the optimal structure of fragment \(\text{F}_3\text{C}-(\text{CF}=\text{CF})_n\text{CF}_3\) is a zigzag chain with bond lengths \(R(\text{C}–\text{C}) = 1.53–1.54\) Å and \(R(\text{C}–\text{F}) = 1.36–1.34\) Å [6] coiling into a helix with an angular pitch of 166.15°, in agreement with the data from [7]. This geometrical model was employed in calculations of the excited states for the compounds of interest. The equilibrium nuclear configuration of each of these compounds has no symmetry elements, whereas, as was noted above, the fragment containing C=C double bonds is nearly plane; hence, the \(C_2\) local symmetry may be assigned to this fragment. In the ground state, the PTFE molecule occurs in the form of a three-dimensional helix with symbol 13/6 [8].
Calculations of Excited Electronic States

The energy of excited electronic states of saturated fluorinated alkyl compounds exceeds $45 \times 10^3$ cm$^{-1}$, and an increase in the number of \(F_3\ell(-\ellF_2-)_n\ellF_3\) units leads to an insignificant shift of the long-wave absorption band. With variation in \(n\) from 8 to 15, the energy of the long-wave transition changes insignificantly (by \(\sim 1000\) cm$^{-1}$), and the oscillator force grows from 0.5 to 1.0. The energy levels of the $S_2$ state are located 3200 cm$^{-1}$ higher than the $S_1$ levels for \(n = 8\); a difference between the energy levels of $S_1$ and $S_2$ states decreases to 1800 cm$^{-1}$ for compounds with \(n = 15\). Given this, the oscillator force for the $S_0 \rightarrow S_2$ transition remains extremely small ($10^{-2}$–$10^{-3}$).

The introduction of a double bond into a C$_{17}$F$_{36}$ molecule (table) naturally decreases the energy of the first singlet transition by 3100–5100 cm$^{-1}$, depending on the place where the double bond appears. The atomic $\pi$-orbitals of the C=C fragment make a substantial contribution to the orbital nature of $S_1$ and $S_2$ states; that is, these states may be defined as the states of the $\pi\pi^*$ type. When a double bond is arranged at the chain end, the lowest electronic state has the $B_u$ local symmetry and the second singlet state possesses the $A_g$ symmetry. At the same time, the oscillator force of the long-wave transition drops by a factor of 2 compared to the saturated compound. However, as the double bond is transferred along the chain, the inversion of the levels takes place: the transition to the $A_g(\pi\pi^*)$ state becomes the lowest with a small oscillator force (0.009). As opposed to the saturated compounds, the second transition occurs near the first transition and an energy difference ranging from 1500 to 700 cm$^{-1}$. For these compounds, absorption falls into the UV spectral region and has almost no effect on the color of PTFE.

Upon introduction of two or more conjugated bonds into the C$_{17}$F$_{36}$ molecule, the $B_u(\pi\pi^*)$ state with the large oscillator force is the lowest in all cases. The energy of the lowest transition of the molecule with two double bonds (table) comprises $32.6 \times 10^3$ cm$^{-1}$ and declines to $18 \times 10^3$ cm$^{-1}$ for the fluoropolyene with six double bonds. Just in this spectral region, the absorption by the color centers detected in [5] (the wavelength range from 300 to 550 nm) is observed (Fig. 1). Thus, our calculations indicate that structures containing no more than six conjugated double bonds are formed in the irradiated PTFE, while the amount of structures with seven or more conjugated bonds is extremely small. However, it should be noted that the energy of the long-wave transition in the studied molecules strongly depends on the structure of the molecule. The ideal case considered above is the planar fragment with conjugated bonds. In the indicated molecules, the length of conjugation is maximal and the corresponding energy of the $S_0 \rightarrow S_1$ transition is minimal. For nonplanar distortions of this fragment, the effective length of conjugation is reduced; as a result, the energy of the long-wave transition is increased. In this case, the long-wave transitions of fluorinated polyenes containing seven or more double bonds fall into the spectral region from 300 to 550 nm.

The experiments on the radiation modification of PTFE performed in [5] were carried out in a medium...