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PHOTOPOLYMERIZATION OF TETRAFLUOROETHYLENE IN SOLUTION OF HEXAFLUOROPROPYLENE TRIMER IN THE PRESENCE OF LONG-LIVED PERFLUOROALLYL RADICALS

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547.413.5'161

A distinctive feature of radiolysis and photolysis of perfluorocarbons is the formation of radicals and anomalously long lifetimes (10^2 - 10^3 h) in the liquid at room temperature. Steric isolation or delocalization of an unpaired electron is the cause which prevents recombination of these long-lived radicals (LR) [1, 2].

Formation of LR of the perfluoroallyl type $(F_3C)_2=C(C_2F_5)\dot{C}FCF_3$ (R_A) takes place in radiolysis of the hexafluoropropylene trimer (HFPT). The concentration of this LR in liquid HFPT changes slightly not only during prolonged storage (up to three years) but also in distillation, dissolution, and heating to 400 K. Photolysis of R_A in the glassy matrix of HFPT results in its phototransformation into other, thermally unstable radical states.

Photopolymerization of tetrafluoroethylene (TFE) in a solution of perfluorinated oils has been initiated by $C_2F_4Br_2$ additives [3]. Photolysis of TFE dissolved in HFPT results in its polymerization, and LR of the perfluoroalkyl type arise in the stage of propagation of the polymer chain [4].

Photopolymerization of TFE dissolved in HFPT in the presence of the long-lived perfluoroallyl radical R_A was investigated in the present study.

EXPERIMENTAL

The perfluoroallyl radical R_A was obtained by radiolysis (^{60}Co γ rays at 300 K) of HFPT containing 90% perfluoro-2,4-dimethyl-3-ethyl-2-pentene and 10% perfluoro-3-isopropyl-4-methyl-2-pentene.

Photolysis of the samples was conducted in quartz ampuls with light from a DRSh-1000 lamp ($\lambda \geq 236$ nm) at room temperature with one intensity of the radiation. The yield of polymer was determined gravimetrically and based on the pressure drop of the TFE during polymerization in an ampul with an attached miniature manometer. The EPR spectra were recorded on a RE-1306 radiospectrometer at 300 K.

RESULTS AND DISCUSSION

The dependences of the yield of polymer in photolysis of a 57 mole % solution of TFE in HFPT (curve 1) and in HFPT undergoing radiolysis and containing $[R_A] = 2.5 \cdot 10^{18} g^{-1}$ (curve 2) are shown in Fig. 1. Note that the initial rate of polymerization of TFE in the presence of R_A is almost one order of magnitude higher than in their absence, and the yield of polymer rapidly attains 100% (conversion was determined on conversion to the initial amount of TFE, and a yield >100% indicates partial incorporation of the HFPT in the macromolecules formed). The R_A present in the solution thus actively sensitize photopolymerization of TFE.

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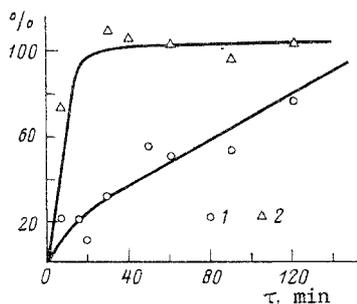


Fig. 1. Dependence of the yield of polymer on the UV irradiation time ($\lambda \geq 236$ nm, 300 K, vacuum) of TFE in HFPT medium (1) and HFPT containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$ undergoing radiolysis (2). Concentration of monomer [TFE] 57 mole %.

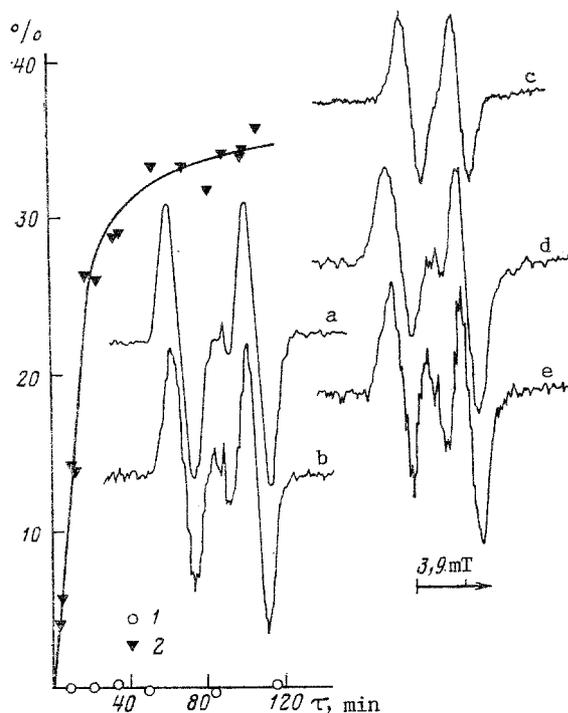


Fig. 2. Dependence of the yield of polymer on the UV irradiation time ($\lambda \geq 236$ nm, 300 K, vacuum) of TFE in HFPT medium (1) and HFPT undergoing radiolysis and containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$ (2). Concentration of monomer [TFE] 9 mole %. EPR spectra of stable radicals formed in photolysis of TFE in HFPT medium for 56 (a), 83 min (b) and in a medium of HFPT undergoing radiolysis and containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$ for 0 (c), 69 (d), and 90 min (e). Concentration of monomer [TFE] 9 mole %.

Prolonged holding of the solution of TFE in HFPT containing R_A at 300 K with no UV irradiation (up to 15 days) does not result in marked polymerization, and there are no qualitative and quantitative changes in the EPR spectra. As a consequence, the perfluoroallyl radical R_A does not directly participate in initiation of polymerization. In photolysis, R_A are transformed into thermally unstable active radicals and it can be hypothesized that they are responsible for the sharp acceleration of photopolymerization of TFE.

The role of R_A is most graphically seen in the experiments with a very small amount of TFE in the solution (9 mole % TFE). In photolysis of a solution of TFE in HFPT of this concentration for 120 min, polymerization could not be observed in general (Fig. 2, curve 1). At the same time, addition of R_A to this solution in the amount of $2.5 \cdot 10^{18} \text{ g}^{-1}$ results in effective polymerization (Fig. 2, curve 2).

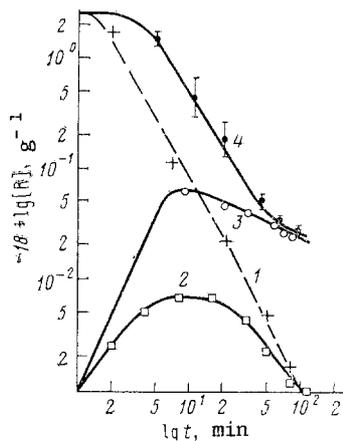


Fig. 3. Change in the concentration of stable radicals as a function of the UV irradiation time ($\lambda \geq 236$ nm, 300 K, vacuum): 1) HFPT containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$ undergoing γ -radiolysis; 2) HFPT; 3) TFE in HFPT medium; 4) TFE in HFPT medium containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$ and undergoing radiolysis. Concentration of monomer [TFE] 9 mole %.

Photolysis of solutions of TFE in HFPT containing R_A results in significant changes in the EPR spectra. The doublet with splitting of 3.9 mT disappears in the EPR spectrum. Other LR with an asymmetric doublet line appear in the EPR spectrum (Fig. 2c, d). The central part of the spectrum appears in the EPR spectrum with an increase in the photolysis time (up to 90 min) (Fig. 2e).

Photolysis of HFPT containing R_A which has undergone radiolysis results in their fast disappearance (Fig. 3, curve 1). A decrease in the concentration of R_A is accompanied by a decrease in the doublet line with $\Delta H_2 = 3.9$ mT in the EPR spectrum, and the distances between the peaks in the doublet increase from 3.9 to 4.6 mT (Fig. 4, curve 1). As noted above, quenching of R_A is due to the phototransformation of this radical into the perfluoroalkyl radical and their subsequent recombination.

The increase in the distance between the peaks in the doublet is apparently due to superposition of another EPR spectrum with greater splitting in the doublet on the doublet spectrum with splitting of 3.9 mT. This spectrum can be assigned to a radical formed in photolysis of HFPT. LR with a doublet line with effective splitting of 3.9–4.6 mT in the EPR spectrum (Fig. 4c) are actually formed in photolysis of HFPT. Superposition of the spectrum of this radical on the spectrum of the remainder of R_A during photolysis results in an increase in the distance between the peaks in the doublet. Accumulation of LR in photolysis of HFPT (see Fig. 3, curve 2) passes through a maximum in 10 min of irradiation (maximum concentration of $6 \cdot 10^{15} \text{ g}^{-1}$). A further increase in the photolysis time to 100 min results in their total disappearance.

LR are also formed in photolysis of solutions of TFE in HFPT. Effective accumulation of LR takes place at the beginning of photolysis of a 9 mole % solution of TFE, and their concentration attains the maximum value of $6 \cdot 10^{16} \text{ g}^{-1}$ in 10 min (cf. Fig. 3, curve 3). The shape of the EPR spectrum of these radicals changes during photolysis. At the beginning of irradiation, a doublet line with $\Delta H_2 = 6.5$ mT is recorded in the spectrum. When the photolysis time is increased to 80 min, the low-intensity central part of the spectrum appears and an asymmetric doublet line is recorded (see Fig. 2a, b). During photolysis, the effective distance between the doublet peaks decreases from 6.5 to 5.7 mT (see Fig. 4, curve 3).

Photolysis of a solution of TFE in HFPT in the presence of R_A can thus be accompanied by the following reactions: 1) phototransformation of R_A into an active perfluoroalkyl radical and its subsequent quenching; 2) initiation of polymerization of TFE by the perfluoroalkyl radicals which are generated in phototransformation of R_A ; 3) formation of LR in photolysis of HFPT; 4) formation of LR in polymerization of TFE in HFPT solution.

The formation of LR during polymerization of a solution of TFE in HFPT takes place more efficiently than in photolysis of pure HFPT. As a comparison of curves 2 and 3 in Fig. 3

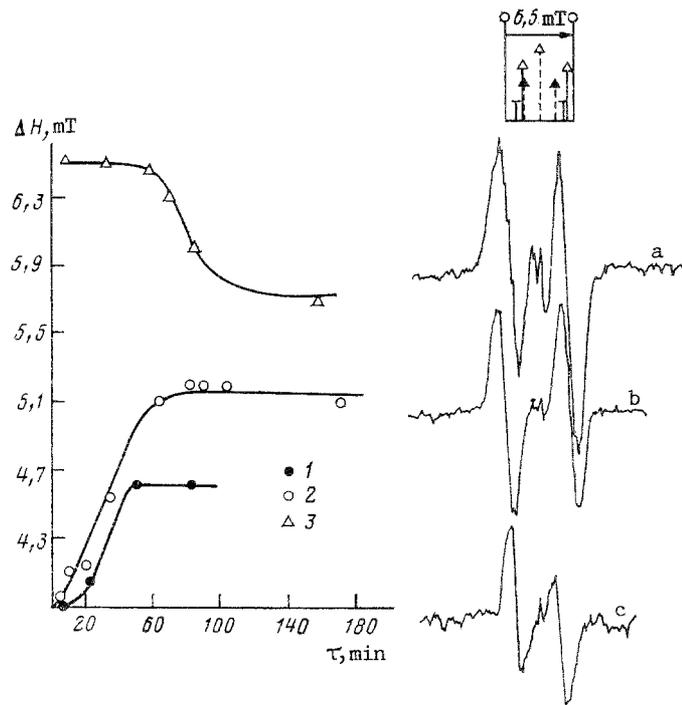


Fig. 4. Change in the effective distance between the peaks in the EPR doublet spectrum formed in photolysis of the following as a function of the UV irradiation time ($\lambda \geq 236$ nm, 300 K, vacuum): 1) HFPT containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$ undergoing radiolysis; 2) TFE in HFPT medium; 3) TFE in HFPT medium undergoing radiolysis and containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$. Concentration of monomer [TFE] 9 mole %. EPR spectra of stable radicals formed during photolysis: a) TFE in medium of HFPT containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$ undergoing radiolysis; b) TFE in HFPT medium for 20 min; c) HFPT for 16 min. Concentration of monomer [TFE] 9 mole %. Theoretical lines of the EPR spectra of LR formed during photolysis of TFE in medium of HFPT undergoing radiolysis and containing $[R_A] = 2.5 \cdot 10^{18} \text{ g}^{-1}$.

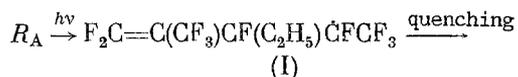
shows, with 100 min of photolysis, the concentration of LR in the system with TFE is more than one order of magnitude greater than the concentration in the system without TFE. During photolysis, the concentration of LR in the TFE + HFPT system is equal to the concentration of LR formed in photolysis of TFE + HFPT + R_A ($[LR] \sim 3 \cdot 10^{16} \text{ g}^{-1}$) (see Fig. 3, curves 3 and 4). The shape of the spectra of the LR in both cases is also identical (see Fig. 2b, e).

During photolysis of TFE in a medium of HFPT containing R_A , an asymmetric doublet line (Fig. 4a) with effective splitting which increases with an increase in the UV irradiation time (Fig. 4, curve 2) appears in the EPR spectrum of LR instead of the doublet line with splitting of $\Delta H_2 = 3.9$ mT (Fig. 2c). The asymmetric doublet line (Fig. 4a) is the superposition of the EPR line of at least four types of radicals: 1) doublet line with $\Delta H_2 = 3.9$ mT from the remainder of the starting perfluoroalkyl radical R_A (Fig. 2c); 2) doublet line with $\Delta H_2 = 6.5$ mT from LR formed in photolysis of TFE in HFPT medium (Fig. 4b); 3) doublet line with $\Delta H_2 = 4.3$ – 4.6 mT from LR formed in photolysis of HFPT (Fig. 4c); 4) triplet line with $\Delta H_3 = 1.6$ mT from LR formed in photopolymerization of TFE in HFPT medium [4].

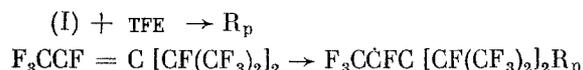
As the theoretical lines in the EPR spectra of these LR show, they differ with respect to the values of the g factor. For this reason, the overall shape of the asymmetric EPR spectrum changes as a function of the relative concentration of these LR. In photolysis for more than 60 min, the fraction of the doublet line with $\Delta H_2 = 6.5$ mT predominates in the overall spectrum.

The following processes leading to the formation or quenching of LR can thus take place in photolysis of TFE in a solution of HFPT containing R_A for up to 200 min.

1. Phototransformation of R_A into an active radical and their recombination

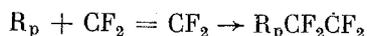


2. Initiation of polymerization by radical (I) and formation of LR of the perfluoroalkyl type during chain propagation in addition of the HFPT molecule to the propagating radical



(doublet with $\Delta H_2 = 6.5$ mT).

Formation of a radical captured by the propagating chain



(triplet with $\Delta H_3 = 1.6$ mT).

CONCLUSIONS

In photolysis of tetrafluoroethylene in a solution of the hexafluoropropylene trimer containing long-lived perfluoroalkyl radicals, the following processes can take place: 1) phototransformation of these radicals into active perfluoroalkyl radicals and their recombination, and participation in initiation of photopolymerization of tetrafluoroethylene; the formation of the long-lived perfluoroalkyl radical on addition of a molecule of solvent to the propagating radical and the formation of a long-lived radical captured by the propagating chain compete with these processes.

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FRAGMENTATION PATHWAYS OF $[(Ph_3P)AuM(CO)_3(\eta^5-C_5H_4CHO)]$ UPON ELECTRON IMPACT IN THE GAS PHASE OR UPON PHOTOLYSIS IN SOLUTION

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A large number of homo- and heterometallic cluster compounds, among them ones containing Au, are currently known. In terms of understanding the factors responsible for the stability and reactivity of these clusters, it is essential that the conversions of these complexes, such as those containing an Au-transition metal bond, be investigated. The chemical properties of these complexes are undoubtedly influenced by the strength of the Au-transition metal bond, which is known to be readily cleaved by the action of different reagents [1]. Since at the present time there is no quantitative data concerning the energy of Au-transition metal bonds in heterobimetallic complexes, it was of interest to us to examine the possible fragmentation pathways for these types of complexes, both upon electron impact (ionization) in the gas phase and upon photolysis in solution. The experiments were carried out with

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