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RADIATION-INITIATED POLYMERIZATION OF FLUOROOLEFINS

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Most fluorinated monomers possess a low polymerization ability both under the influence of initiators of the usual type and under the influence of radiation. In the latter case, oligomers are usually formed with small radiation-chemical yields; these are unsaturated liquid compounds (^{1}).

A possible reason for such behavior of fluoroolefins is the electron depletion of the π-bond, caused by the strong electron-attracting action of the CF_3 group, and conjugation of the double bond with the C$-$F bond, which has a pronounced tendency toward conjugation.

For the same reason, but as a result of the electron-attracting action of the entire fluorocarbon chain, the radical $\sim CF_2-CF-CF_2\sim$, formed upon irradiation of polytetrafluoroethylene, is less active than the radical $\sim CF_2-CF_2$ (^{2}).

From this point of view, the polymerization of certain fluoroolefins studied in the present work (see Table 1) upon irradiation with γ-rays from Co^{60} in "bulk" at 20-25° in ampoules (dilatometers) made of molybdenum glass is considered.

The influence of the CF_3 group on the polymerization of fluoroolefins is especially noticeable when tetrafluoroethylene and perfluoropropylene are compared. It is known that upon irradiation of perfluoropropylene, liquid products (3-4-mers) are formed, constituting a mixture of compounds with unsaturation of the type $CF_2=CF-$ and $-CF=CF-$, as well as with a cyclic structure (^{1,3}). The radiation-chemical yield of the indicated oligomers, equal to $\sim$10 molecules per 100 eV (based on monomer consumption), indicates the weakly expressed chain character of the radiation polymerization of perfluoropropylene. Attempts to polymerize perfluoropropylene by an ionic route also lead to the formation of unsaturated oligomers (^{4}).

It is most probable that the formation of radicals upon irradiation of perfluoropropylene in the liquid phase occurs by abstraction of a fluorine atom from the CF_3 group, in which it is chemically mobile (^{5}). The presence in the oligomers formed of $CF_2{=}CF-$ groups, detected from IR spectra, indicates that the radicals $CF_2{=}CF-CF_2$ participate either in initiation or in termination of kinetic chains.

Termination of the polymerization chain upon irradiation of perfluoropropylene in "bulk" may also occur through interaction of the polymer radical with a fluorine atom:

$$R_F-(CF_3)\dot{C}F + F \rightarrow \dot{R}F-\dot{C}F(CF_3) + F_2,$$

since the formation of oligomers upon irradiation of perfluoropropylene proceeds with loss of fluorine (3). The interaction of free electrons delocalized in the fluorocarbon radical (6) leads to the formation of internal double bonds and to cyclization of the fluorocarbon chain, which inhibits chain growth.

The introduction of hydrogen into the perfluoropropylene molecule has a great influence on the polymerization of fluoroolefins of this series.

Table 1

Monomer	Irradiation intensity, r/sec	Radiation-chemical yield of polymer, molecules/100 eV	Molecular weight of polymer	Conversion, %	Polymer characteristics
2,3,3,3-tetrafluoropropene-1$CH_2{=}CF-CF_3$	30	350	$\sim 700^2$	100	Crystals; partially soluble in acetone; m.p. 90° C; unsaturation; 6–7 units
2,3,3,3-tetrafluoropropene-1$CH_2{=}CF-CF_3$	250	–	$\sim 700^3$	–	Powder; soluble in acetone and monomer; unsaturation; 6–7 units

Monomer	Irradiation intensity, r/sec	Radiation-chemical yield of polymer, molecules/100 eV	Molecular weight of polymer	Conversion, %	Polymer characteristics
1,2,3,3,3-pentafluoropropene-1$CFH=CF-CF_3$	30	88	~ 800[4]	25	Wax-like substance; soluble in acetone and monomer; unsaturation; 6-mer
1,2,3,3,3-pentafluoropropene-1$CFH=CF-CF_3$	95	46	–	16	Same
1,1,3,3,3-pentafluoropropene-1$CF_2=CH-CF_3$	25	9	520[5]	5	Viscous liquid; unsaturation; 4-mer
1,1,3,3,3-pentafluoropropene-1$CF_2=CH-CF_3$	150	13	510[5]	7	Same
3,3,3-trifluoro-2-trifluoromethylpropene-1$CH_2=C(CF_3)_2$	17	21	580	6	Viscous liquid; unsaturation; 3-4-mers
3,3,3-trifluoro-2-trifluoromethylpropene-1$CH_2=C(CF_3)_2$	110	16	690	16	Same

[1] Calculated from monomer consumption. [2] Calculated from absorbed energy and radiation-chemical yield. [3] Estimated from characteristic viscosity. [4] Calculated from the decrease in intensity of the absorption band in the IR spectrum corresponding to the double bond (1730 cm^{-1}). [5] Determined cryoscopically in Freon-112.

Table 1 presents data characterizing radiation-initiated polymerization of several fluoroolefins. The corresponding kinetic curves are shown in Fig. 1.

Judging from the IR spectra, all oligomers contain double bonds present in the monomer molecules, i.e., located at the ends of the oligomer molecules. The radiation-chemical yields of the oligomers indicate a noticeable occurrence of chain processes. At the same time, comparison of these yields, the nature of the oligomers formed, and the dependences of the polymerization rates on irradiation intensity indicates a connection between polymerizability and the position of hydrogen in the molecule. The values of n in the equations $v = kJ^n$ for the initial period of polymerization are, respectively (in the order given in Table 1), 0.4; 0.8; 1.7 (1.3), and 1.

Polymerization of 2,3,3,3-tetrafluoropropene-1 proceeds most readily. The value of n indicates bimolecular termination of the free-radical chain reaction. In this case, apparently, the relative ease of polymerization is due to the absence of conjugation of the double bond with the C—F bond in position 1. The presence of a C—F bond in position 1 results in a significant decrease in the polymerizability of 1,2,3,3,3-pentafluoropropene-1. In this case, during chain growth, inhibitory processes of the same type as in the case of perfluoropropylene may possibly begin to occur.

The C—F bond in position 2 does not exert a large influence on the polymerization of perfluoroolefin, since the radiation-chemical yields of the oligomers formed upon irradiation of perfluoropropylene and 1,1,3,3,3-pentafluoropropene-1, as well as their character, are approximately the same. The most interesting feature of the polymerization of 1,1,3,3,3-pentafluoropropene-1 is that in the initial period of irradiation it proceeds according to the law $v \sim J^{1.7}$, and then $v \sim J^{1.3}$. This kinetic feature may be due to the occurrence of side radiation-chemical processes not associated with chain growth—

chemical processes that are determined by a considerably greater conjugation effect of the double bond with the substituent CF_3 than with the $C—F$ bond in position 2.

The possibility of side radiation-chemical transformations inhibiting polymerization, including transformations of the accumulating polymer, is the main reason why, under prolonged irradiation, in all three cases a decrease in the polymerization rate is observed. In the case of 1,2,3,3,3-pentafluoropropene-1 and 1,1,3,3,3-pentafluoropropene-1 this decrease occurs already at a very small degree of polymerization (see Fig. 1). The polymerization of 2,3,3,3-tetrafluoropropene-1 (at an irradiation intensity of 30 r/sec) proceeds at a constant rate up to a conversion of $\sim 80\%$. Judging from the nature of the polymer formed, it may be concluded that this phenomenon is due to crosslinking of the polymer formed under the action of radiation, along with polymerization of the monomer.

Fig. 1. Dependence of the volume contraction of the liquid phase upon irradiation of monomers at various irradiation intensities.

Fig. 1

Figure 1: Fig. 1

a —2,3,3,3-tetrafluoropropene-1; *b* —1,2,3,3,3-pentafluoropropene-1; *v* —1,1,3,3,3-pentafluoropropene-1; *g* —3,3,3-trifluoro-2-trifluoromethylpropene-1

One of the reasons for the formation of low-molecular-weight products upon irradiation of fluoroolefins may be disproportionation of polymer radicals with perfluorinated radicals, which have low diffusional capacity. Such a phenomenon apparently occurs in the radiation-initiated polymerization of 3,3,3-trifluoro-2-trifluoromethylpropene-1. The formation of initiating radicals in this case occurs by detachment of the group $-CF_3$, which has a pseudohalogen character, since in the EPR spectrum of this monomer irradiated at 77 K there are 4 lines of hyperfine structure that may be assigned to the radical $\dot{C}F_3$. Chain scission during polymerization of 3,3,3-trifluoro-2-trifluoromethylpropene-1 may occur in the local volume of the "polymerization cage" through interaction of the radical $\dot{C}F_3$, capable of abstracting hydrogen atoms, with the polymer radical

$$\sim CH_2 - (CF_3)_2\dot{C} + \dot{C}F_3 \rightarrow \sim CH = C(CF_3)_2 + CF_3H,$$

which explains the possible formation of an internal double bond and also confirms the kinetic dependence indicated above, $v \sim J^1$.

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