
RADIATION CHEMISTRY OF THE FLUOROOLEFINES

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The authors and their co-workers have shown that the fluoroolefins undergo extensive high-yield radical polymerization under $\beta$ and $\gamma$ irradiation. Low-yield radiolysis of the fluoroolefins also occurs here.

Radiational polymerization of the fluoroolefins is of interest since polymerization does not require the presence of chemical initiators in the system; initiation occurs at low temperatures; polymerization takes place in the solid monomer; and in certain cases, the monomer in question can be polymerized only with difficulty by other methods.

We have undertaken an extensive study of the radiation chemistry of the lower fluoroolefins with the aim of making known the possibilities of synthesizing fluorine-containing monomers and, at the same time, examining the chemical behavior of compounds of this type under irradiation. Study has been made of the radiolysis, homopolymerization, copolymerization, and graft copolymerization of the fluoroolefins.

Study has also been made of the macromolecules responsible for chain extension in the polymerization of tetrafluoroethylene (TFE). The kinetics of the radiational homopolymerization of TFE, trifluorochloroethylene, trifluoroethylene, vinyldiene fluoride, and vinyl fluoride have been investigated. The structures and properties of the resulting polymers have also been studied.

The results of these studies have been published in a series of articles [1-20]. The most detailed studies have been carried out on the heterogeneous radiational polymerization of TFE, in the gaseous and liquid phases and under the excess pressure of the monomer.

It was first shown that TFE is readily polymerized under $\beta$ and $\gamma$ irradiation. The radiochemical yield in the homopolymerization of TFE is one or two orders higher than the yields met in the homopolymerization of other unsaturated compounds, values as high as $I = 1 \times 10^6$ mole/100 eV being observed here.

TFE is readily polymerized, with extremely high radiochemical yield, under $\gamma$ irradiation, so readily, in fact, that this monomer can be polymerized in the gaseous phase at atmospheric pressure and 20°C, or in the liquid phase at $-78^\circ$C.

Hexafluoropropylene polymerizes much more slowly than TFE. A radiochemical yield of only 13 mole/100 eV is attained when this compound is irradiated at 20°C and a dose rate of 10 rad/sec. Complete polymerization (above 90%) of the monomer is attained only after irradiation for 300 h at a dose rate of 600 rad/sec. The product obtained from this type of reaction is a complex liquid oligomer with molecular weights in the 300-4000 range.

Irradiation to a dose of 250 Mrad at a dose rate of 600 rad/sec brought about no detectable change in perfluoroisobutylene.

Liquid-phase irradiation of trifluorochloroethylene at 20°C and a dose rate of 10 rad/sec led to the formation of a solid polymer, the radiochemical yield of the process being $5.5 \times 10^3$ mole/100 eV.

Studies on mass radiational polymerization were carried out with trifluorochloroethylene and trifluoroethylene. Radiational polymerizations of vinyldiene fluoride and vinyl fluoride...
TABLE I. Results of a Study of the Radiational Polymerization of Fluoroethylenes and Ethylene

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Time of irradiation, min</th>
<th>Dose, rod</th>
<th>Polymerization rate $\nu$ $%$/min</th>
<th>mole/(liter$\cdot$min)</th>
<th>1, mole/100 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_2$=CF$_2$</td>
<td>4</td>
<td>6.10$^5$</td>
<td>2.0</td>
<td>0.23</td>
<td>3.56.10$^3$</td>
</tr>
<tr>
<td>CF$_2$=CFH</td>
<td>24</td>
<td>1.4.10$^6$</td>
<td>0.083</td>
<td>0.01</td>
<td>1.82.10$^6$</td>
</tr>
<tr>
<td>CF$_3$=CH$_2$</td>
<td>40</td>
<td>2.4.10$^6$</td>
<td>0.030</td>
<td>0.006</td>
<td>1.4.10$^6$</td>
</tr>
<tr>
<td>CFH=CH$_2$</td>
<td>84</td>
<td>5.10$^6$</td>
<td>0.023</td>
<td>0.003</td>
<td>9.2.10$^5$</td>
</tr>
<tr>
<td>CH$_2$=CH$_2$</td>
<td>676</td>
<td>4.0.10$^6$</td>
<td>0.003</td>
<td>0.0004</td>
<td>1.9.10$^5$</td>
</tr>
</tbody>
</table>

were carried out in mass, and in various organic solvents. Studies on the kinetics of radiational polymerization were carried out in the beginning, and in the advanced stages, of the polymerization process.

The kinetic studies led to estimates of the rates of polymerization of various fluoroethylenes, and the dependence of these rates on the nature of the monomer; they also established the mechanisms of these complex heterogeneous processes, and marked out a number of their characteristic features.

The experimental data obtained in this work were used as a basis for certain theoretical studies of the effect of the fluorine atom on the heterogeneous polymerization of the fluoroethylenes. The principal results obtained here will be outlined in the present paper.

Table 1 shows the results on the radiational polymerization of TFE, trifluoroethylene, and vinyl and vinylidene fluorides, in mass and in the initial states of conversion (up to 2%) where the effect of the polymer was still negligibly small.

Data on the radiational polymerization of ethylene under similar conditions are given for comparison. Experiments were carried out in dilatometers, working at 0°C and a dose rate of 10 rad/sec.

The figures of Table 1 show that the polymerization rates of the various compounds were quite different from one another. TFE had the highest polymerization rate, and ethylene the lowest.

The data on polymerization rates indicated that successive reduction in the number of fluorine atoms in the molecule reduced the activity of the compound in polymerization, the ordering of the olefins in this respect being given by the series:

$$\text{CF}_2=\text{CF}_2 > \text{CF}_2=\text{CFH} > \text{CF}_2=\text{CH}_2 > \text{CFH}=\text{CH}_2 > \text{CH}_2=\text{CH}_2$$  (1)

Interest naturally attached to this effect of the fluorine atom on the heterogeneous polymerization of these compounds.

Analysis of the data of the literature on the chemical and physicochemical properties of the fluoroethylenes showed that the presence of the fluorine atoms gave rise to differences in the behavior of the double bonds in these compounds. The fluorine exerts an inductive effect on the C=C π-bond, and enters into conjugation with its electrons.

The presence of fluorine atoms in the molecules of the fluoroethylenes increases the vibration frequency of the C=C bond, and reduces the distance of a separation of the atoms in this bond, the strength of the bond increasing as the number of fluorine atoms is increased [21, 22]. This would seem to be in direct contrast to the double-bond energies reported for ethylene and tetrafluoroethylene. In fact, the data of [23, 24] indicate that the energy of bonding in ethylene (142 kcal/mole) is considerably higher than the energy of bonding in tetrafluoroethylene (105 kcal/mole). Attempts to resolve this contradiction by drawing on inductive effects alone [25] lead to the conclusion that the energy of C=C bonding should be the same in ethylene and tetrafluoroethylene, a result inconsistent with the data of [21, 22].

Thus, the data on the energy of C=C bonding in ethylene and tetrafluoroethylene are contradictory and untrustworthy.

Considerable interest attaches to the results of quantum-chemical calculations on the