Application of perfluoroacylfluorides in the synthesis of perfluoroalkylvinyl ethers IV.

Synthesis of bifunctional oligomers of tetrafluoroethylene oxide.

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Frost resistance increase is an important problem in chemistry of fluoropolymers. One of the ways of solving this problem is introduction of oxygen atoms into fluoropolymers that allows reducing significantly the glass transition temperature of these thermally stable and chemically inert compounds.

The methods of synthesis of monomers for creation of fluoropolymers with a reduced glass transition temperature [1,2] and the dependence of the frost resistance of the fluoropolymers on the structure of polyfluoroalkylvinyl ethers was discussed in previous papers [3]. This paper gives a method to synthesize bifunctional oligomers of tetrafluoroethylene oxide from which polyperoxides were produced used in the process of radical copolymerization of the monomers as initiators and influenced on the glass transition temperature of the polymer formed.

To produce bifunctional oligomers of tetrafluoroethylene oxide (TFEO), a rotary absorber was charged with a solution of potassium alkoxide $\text{KO}_2 \text{CF}_2 \text{COF}$ in diglyme which was preliminarily obtained by the reaction of perfluoromalonyl fluoride with potassium fluoride:

$$\text{FOCCF}_2 \text{COF} + \text{KF} \rightarrow \text{KO}_2 \text{CF}_2 \text{COF}$$

The rotary absorber was joined to a reactor of photo-chemical oxidation of tetrafluoroethylene (TFE) and at a temperature of -10 to -30°C a mixture of oligomeric products was obtained:

$$\text{FOCCF}_2 \text{O} \text{CF}_2 \text{O} \text{CF}_2 \text{COF} \quad m + n = 0, 1, 2, 3, \ldots \quad (A) \quad (85-90\%)$$

$$\text{CF}_3 \text{O} \text{CF}_2 \text{COF} \quad n = 0, 1, 2, 3, \ldots \quad (A) \quad (10-15\%).$$

On the basis of diacylfluorides (A) a number of diacylchlorides was synthesized:

$$\text{FOCCF}_2 \text{O} \text{CF}_2 \text{O} \text{CF}_2 \text{COCl}$$

A flask was charged with 137 g of a mixture of dimethyl ethers of dicarbonic acids of the general formula:

$$\text{MeOOCF}_2 \text{O} \text{CF}_2 \text{O} \text{CF}_2 \text{COOMe}$$

with $n+m=3$ and 25 mL of 85% fomic acid was added and heated at 160°C. The fomic acid was distilled and 124 g of dicarbonic acid was discharged. The yield was 94%. The acids with $n+m=4$ and $n+m=5$ were obtained in a similar way.

Experimental

Synthesis of diacylchloride B with $n+m=3$ of the following formula:

$$\text{ClOCCF}_2 \text{O} \text{CF}_2 \text{O} \text{CF}_2 \text{COCl}$$

A flask was charged with 137 g of a mixture of dimethyl ethers of dicarbonic acids of the general formula:

$$\text{MeOOCF}_2 \text{O} \text{CF}_2 \text{O} \text{CF}_2 \text{COOMe}$$

with $n+m=3$ and 25 mL of 85% fomic acid was added and heated at 160°C. The fomic acid was distilled and 124 g of dicarbonic acid was discharged. The yield was 94%. The acids with $n+m=4$ and $n+m=5$ were obtained in a similar way.
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Then 85g of PCl₅ was charged into a flask and 87g of dicarbonic acid with $n+m=3$ was added dropwise. Termination of hydrogen chloride evolution was an evidence of the reaction completion. After distillation of POCl₃ and vacuum rectification there was produced 85g of diacyl chloride B with $n+m=3$. (b.p.82°C/1 Torr) (table). The yield was 96.6%. The diacylchlorides with $n+m=4$ and $n+m=5$ were obtained similarly, the analytical data are presented in the Table.

Table

<table>
<thead>
<tr>
<th>Formula</th>
<th>B.p./Torr</th>
<th>ν₂⁰</th>
<th>d²⁰</th>
<th>General formula</th>
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<tbody>
<tr>
<td>A *</td>
<td>82/1</td>
<td>1,3070</td>
<td>1,7225</td>
<td>C₁₃F₂₂O₇Cl₂</td>
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<td>B (m+n=4)</td>
<td>126/10</td>
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<td>1,7535</td>
<td>C₁₅F₂₆O₈Cl₂</td>
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<td>B (m+n=5)</td>
<td>125/2</td>
<td>1,3042</td>
<td>1,7665</td>
<td>C₁₇F₃₀O₉Cl₂</td>
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</table>

* ClOCCF₂(CF₂CF₂)₃O(CF₂)₃OCF₂COCl

References