A New Intermediate for the Production of Flexible Stable Polymers

The problem:
A number of polyimides have been prepared and studied for use as high-temperature, solvent-resistant sealants. Some of the most promising candidates have included aryl-fluorocarbon groups to increase the solvent resistance of the polymer. Dianhydride intermediates of the form

\[ \text{(CF}_2\text{)}_n \text{OC} \quad \text{(I)} \]

have been used in the synthesis, but the resulting polymers are insufficiently flexible for use as sealants.

The solution:
A method of incorporating ether linkages into the perfluoroalkylene segment of dianhydride (I) above yields an intermediate that may be used in the synthesis of more stable polyimides having increased flexibility.

How it’s done:
The synthesis yields ether-linked aryl tetracarboxy dianhydrides of the structure:

\[ \text{(II)} \]

The synthesis steps are outlined below:

\[ \text{CF}_3\text{-}\text{OH} + \text{CIC} \quad \text{(CF}_2\text{)}_3\text{CCl} \rightarrow \]

The acid chloride-hydroxyl group reaction and the \( \text{SF}_4 \) fluoridation are fairly straightforward. However, the preferential hydrolysis of the aryl-\( \text{CF}_3 \) to \( \text{COOH} \) without attack on the aryl-\( \text{OCF}_2 \) linkage, the essential feature of the synthesis, has not previously appeared in the literature.

The effect of the ether linkage on polyimides incorporating structure II may be seen in the change in the glass transition temperature. Polyimides with structure I have transition temperatures in the range of 60 to 65° C; those with structure II in the range of 40 to 45° C.

(continued overleaf)
Note:
No further information is available. Specific questions, however, may be directed to:
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Patent status:
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