New perfluoroalkyl polytriazines containing pendent iododifluoromethyl groups are prepared by the reaction of perfluoroalkyl dinitriles with ammonia to form poly(imidoylamidines), followed by the cyclization of the imidoylamidine groups with, e.g., various mixtures of a perfluoroacyl fluoride with an o-iodoperfluoroacyl fluoride. The polytriazines obtained can be cured by heat which causes crosslinking at the iododifluoromethyl groups by elimination of iodine and formation of carbon-to-carbon bonds.
THERMOGRAVIMETRIC ANALYSIS OF THE CURED PRODUCT OF EXAMPLE 3.
SAMPLE WEIGHT: 17.25 mg; ATMOSPHERE: N$_2$; HEATING RATE: 10 °C/min.
PERFLUOROALKYL POLYTRIAZINES CONTAINING PENDENT IODODIFLUOROMETHYL GROUPS

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to perfluoroalkyletriazine polymers and more particularly to a new method for preparing them.

2. Description of the Prior Art

Perfluoroalkyletriazine polymers have been prepared heretofore by two different methods, namely the acylationcyclodehydration of imidoylamidines and the free radical coupling of preformed triazine derivatives. However, these polymerization methods have so far yielded polymer specimens that show disappointing sensitivity to reaction conditions, afford poor reproducibility, and yield polymers of molecular weights only marginally high enough for good physical properties". (Fluoropolymers, page 288. In fact, this approach is said to fail "because the ammonia liberated during cyclization causes reorganization reactions, randomizing the assimilation of mono- and difunctional compounds into triazine rings, altering the functionality of the reaction system, and leading to undesired cross-linking and shortened chains". (Fluoropolymers, page 276.) As to the second method, coupling of preformed triazine rings, synthetic difficulties and poor reactivity have led to polymers that are not elastomeric at room temperature, due to the shortness of the chains between the triazine rings (Fluoropolymers, page 280). In the circumstances, the principal object of the present invention is to provide a method that overcomes some of the shortcomings of the prior art and yields triazine polymers that are elastomeric at ambient temperature.

SUMMARY OF THE INVENTION

It has now been discovered that new linear perfluoroalkyl polytriazines with pendant difluoroiodomethyl groups can be synthesized and thus crosslinked by reaction of the pendant groups under the influence of heat, ultraviolet radiation or conventional metal catalysts.

BRIEF DESCRIPTION OF THE DRAWING

The FIGURE is a plot of the weight loss of a cured polytriazine of the invention against temperature as determined by thermogravimetric analysis.

DETAILED DESCRIPTION OF THE INVENTION

The new linear polytriazines of the invention are prepared by the following reaction sequence:
employed is desired. Sodium fluoride may be used to
remove the hydrogen fluoride formed in the reaction.
The linear polytriazines of the invention can be
crosslinked by reaction of their difluorodimethyl
the activity, 10 g, was added to complete the
reaction and the mixture was stirred for several hours.
The reaction mixture was washed repeatedly with
water to remove the acids formed. The organic layer
was separated, dissolved in 1,1,2-trichlorotrifluoro-
ethane and passed over a column of neutral alumina to
remove any traces of acid. The solvent was removed
under vacuum leaving 32 grams of the polytriazine.

EXAMPLES 3 TO 8

A series of triazine fluorooether polymers were
prepared with m+n values of 2 to 6 and an iodo-
containing side chain fraction \( \frac{R_2^{2}COF}{R_2^{2}COF+R_1^{2}COF} \) of
0.05 to 0.15. The procedure employed was essentially
that already described in Example 2, and the prepara-
tion characteristics of each polymer as well as some of
its properties are summarized in the table below. The
linear polytriazines were cured by heating at 160° C. for
4 days, followed by heating at 215° C. in a glass vial for
20 to 100 hours. Modulus was measured on a du Pont
943 thermomechanical analyzer and thermal data was
obtained from a du Pont 990 thermal analyzer.

<table>
<thead>
<tr>
<th>Example m + n</th>
<th>I-Chain Fraction</th>
<th>Core Modulus at 215° C.</th>
<th>Approx. Modulus (dynes/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2 0.08</td>
<td>-35° C.</td>
<td>8 x 10⁶</td>
</tr>
<tr>
<td>4</td>
<td>2 0.05</td>
<td>-37° C.</td>
<td>3 x 10⁶</td>
</tr>
<tr>
<td>5</td>
<td>2 0.12</td>
<td>-37° C.</td>
<td>8 x 10⁶</td>
</tr>
<tr>
<td>6</td>
<td>4 0.05</td>
<td>-41° C.</td>
<td>4 x 10⁶</td>
</tr>
<tr>
<td>7</td>
<td>4 0.08</td>
<td>-41° C.</td>
<td>5 x 10⁶</td>
</tr>
<tr>
<td>8</td>
<td>6 0.15</td>
<td>-45° C.</td>
<td>3 x 10⁶</td>
</tr>
</tbody>
</table>

The thermal stability of a typical crosslinked polytria-
zine elastomer (Example 4) is shown in the accompa-
nying FIGURE. Before extraction, the thermogravimetric
analysis showed a 1% weight loss at 350° C. and after
extraction, the 1% weight loss shifted to 420° C. The
potential thermal stability of the poly(triazine
fluoroether) elastomer is indicated by the excellent ther-
momechanical data for the extracted sample. The same material,
when tested for isothermal weight loss, showed the
following results.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>% Weight Loss/Hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>375° C.</td>
<td>0.8%</td>
</tr>
<tr>
<td>400° C.</td>
<td>4</td>
</tr>
<tr>
<td>425° C.</td>
<td>8</td>
</tr>
</tbody>
</table>

The o-iodoperfluoroacetyl fluorides were prepared in
the following manner, starting from the appropriate
hexafluoroalkylene oxide-oligomer acyl fluoride.

Diglyme, 65 ml, sodium carbonate, 16 g (0.15 mole),
and iodine, 15 g (0.06 mole), were added to a three-
necked flask equipped with magnetic stirrer, thermo-
meter, condenser, and dropping funnel. Hexafluoropropyl-
enic oxide-pentamer acyl fluoride, 23.8 g (0.03 mole),
was added slowly through the dropping funnel to the
stirred slurry. After completion of the addition, the
mixture was heated to 140°-160° C. for one hour. After
cooling to room temperature, the reaction mixture was
poured into iced water and the product, 20.5 g, separated as the heavy phase. This product was a mixture of C₃F₇O[CF(CF₃)CF₂O]₃CFICF₃ (66.8%) and a second component (32.4%), shown to be by NMR and IR spectra a mixture of the vinyl ether and the hydroether. Distillation of the product mixture yielded the pure alkyl iodide (boiling point 60°C/0.3 mm). The IR and NMR spectra, as well as the carbon and fluorine contents, were consistent with the alkyl iodide structure given above.

The crosslinked polymers prepared by the method of this invention are tough, elastic, heat and chemical resistant substances which can be used in many demanding applications such as fuel tank sealants, O-rings, wire enamels, pneumatic ducts and edge close-outs in aircraft, and so on. Other uses for the products, as well as variations in the materials and procedures disclosed, can be devised by the man skilled in the art without departing from the spirit of the invention as described by the following claims.

What is claimed is:

1. A linear polytriazine curable to a crosslinked elastomer and consisting of randomly distributed repeating units of the formula

\[
\begin{align*}
\text{N} & \text{N} \\
\text{Rf}^1 & \text{Rf}^2 \\
\text{Rf} & \text{Rf}
\end{align*}
\]

and

\[
\begin{align*}
\text{N} & \text{N} \\
\text{Rf}^1 & \text{Rf}^2 \\
\text{Rf} & \text{Rf}
\end{align*}
\]

wherein:

(a) \text{Rf} represents identical bivalent perfluorinated organic radicals or any combination of bivalent perfluorinated organic radicals, said radicals being selected from the group consisting of

\[(\text{CF}_2)_p\]

in which \(p\) ranges from 2 to 18, and oligomeric or polymeric radicals prepared by the reaction of a perfluorinated dicarboxylic acid halide with a perfluoroperoxide and having the formula

\[-\text{CFY(OCFCF}_2\text{O})_m\text{O(CF}_2\text{O})_n\text{O(CFYCF}_2\text{O})_m\text{CFY-}\]

wherein \(Y\) is a fluorine atom or a trifluoromethyl group, \(p\) ranges from 2 to 18, and \(m + n\) ranges from 2 to 7;

(b) \text{Rf}^1 represents a monovalent perfluoror radical selected from the group consisting of (1) monovalent perfluorinated alkyl radicals containing up to 11 carbon atoms, (2) monovalent perfluorinated alkyether radicals having the formula \(\text{Rf}^2\text{O(OCFCF}_2\text{O})_m\text{CFY-}\) in which \(\text{Rf}^2\) is a perfluorinated alkyl group containing up to 3 carbon atoms, \(Y\) is a fluorine atom or a trifluoromethyl group, and \(y\) ranges from 0 to 50, and (3) mixtures thereof;

(c) \text{Rf}^2 is a monovalent \(\omega\)-iodoperfluoro radical selected from the \(\omega\)-ido substituted homologs of \(\text{Rf}^1\); and

(d) the number of iodine-containing randomly distributed triazine repeating units constitutes from about 1 to 100% of all repeating units in the linear polytriazine compound.

2. The polytriazine of claim 1 wherein \(p\) ranges from 2 to 10, and \(y\) ranges from 0 to 15.

3. The polytriazine of claim 1 wherein the proportion of \(\omega\)-iodoperfluororadicals to iodine-free perfluororadicals ranges from about 5:95 to 15:85.

4. The polytriazine of claim 1 wherein the number of iodine-containing randomly distributed repeating units constitutes from about 5 to 15% of all repeating units in the linear polytriazine compound.

* * * * *

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