Alpha, omega-perfluorodicarboxylic acids.

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This invention relates to a controlled free radical oligomerization of tetrafluoroethylene and a means of introducing carboxylic acid functionality at the ends of each chain.

Synthetic routes to perfluorocarboxylic acids have commonly involved the oxidative cleavage of carbon — carbon double bonds such as those present in perfluorocycloalkenes or perfluorodiolifins. The free radical polymerization of tetrafluoroethylene to give high molecular weight insoluble and somewhat intractable polymer is known. The use of aqueous peroxydisulfate as an initiator has been shown to produce high molecular weight insoluble polymers is also known. However, the established use of free radical initiator concentrations for tetrafluoroethylene is substantially below 0.5% by weight of the reaction medium, and preferably below 0.1% by weight.

The paper by K. L. Berry and J. H. Peterson, J. Am. Chem. Soc., 73, 5195 (1951) describes the free radical polymerization of tetrafluoroethylene using aqueous peroxydisulfate in concentrations of about 0.05% by weight, and farrous iron concentrations of about 2 parts per million. However, this polymerization of tetrafluoroethylene produced a high molecular weight insoluble and somewhat intractable polymer with number average molecular weight of about 142,000 to about 534,000.

The paper by M. I. Bro and C. A. Sperati, J. Polymer Sci., 38, 289 (1959), also describes the use of aqueous peroxydisulfate initiator for the polymerization of tetrafluoroethylene which produced only high molecular weight polymer (350,000 to 2,150,000 g/m). Concentrations of the peroxydisulfate were low, and ranged from about 0.2 to about 0.4% by weight. Furthermore, only a small amount of the peroxydisulfate was consumed because the polymerization was performed in the absence of any free radicals. Other papers describe the synthesis of a,ω-perfluorocarboxylic acids wherein n = 4, 6, 8, 12 (I. L. Kunyants, Chih-Yuan Li, and V. V. Shokina (Chem. Abs. 56, 302 (1962))); and wherein n = 3, 4, (E. T. McBee, P. A. Wiseman, and D. D. Bachmann, Ind. Eng. Chem., 39, 415 (1947)). However, none of the above references describe the use of relatively high, above 5% by weight, free radical initiator concentrations for the synthesis of a,ω-perfluorocarboxylic acids and the mixtures formed thereby, by the methods of the present invention.

It is therefore an object of the present invention to provide a synthesis of a,ω-perfluorocarboxylic acids via a controlled free radical oligomerization reaction.

It is a further object of this invention to produce mixtures of said a,ω-perfluorocarboxylic acids of both even- and odd-numbered chain lengths.

It is a further object of this invention to use high concentrations of free radical initiators in order to control oligomerization.

The foregoing and other objects, advantages and features of this invention may be achieved by reacting tetrafluoroethylene with at least 0.5% by weight of a peroxydisulphate salt in an aqueous environment, thereby producing oligomeric a,ω-perfluorocarboxylic acids of even- and odd-numbered chain lengths of the general formula HOOC(CF₂)nCOOH, wherein n = 1 to about 1000. A metal ion promoter is preferably used to assist the decomposition of the peroxydisulphate salt. The reaction is preferably carried out in the range of about 35°C to about 100°C. Performed in this manner, this method provides a facile route to perfluorocarbon chains with a,ω-carboxylic acid functionality. These products are strongly acidic and are of useful starting materials for producing polymers such as polyurethanes, polyamides and polybenzimidazoles. Tetrafluoroethylene is treated in an aqueous environment with at least 0.5% by weight of a peroxydisulphate salt. The rate of decomposition to hydroxyl radicals of the peroxydisulphate salt can be readily controlled using promoters at specific temperature ranges. Sodium, potassium, and ammonium peroxydisulfates are preferred because of their relatively high solubility in water.

It is desirable, but not essential, to use a metal ion promoter to activate and control the decomposition of the peroxydisulphate salt at temperatures in the range from about 0°C to about 100°C. Thermal decomposition of peroxydisulphate proceeds slowly, if at all, in this temperature range in the absence of a promoter. Typical promoters are ions of polyvalent metals which readily undergo oxidation — reduction wherein the metal is reactions selected from the group comprising iron, nickel, cobalt and copper.

The combination of peroxydisulphate with promoter in an aqueous media allows the use of relatively low reaction temperatures, namely from about 35°C to about 100°C, in order to control the rate of hydroxyl radical formation. If the temperature is below about 35°C, radical formation will be slow, and limited amounts of lower oligomeric products will be formed.

The reaction of tetrafluoroethylene in an aqueous medium with the peroxydisulphate salt is conveniently carried out in pressure vessels such as stirred autoclaves operated in batchwise or continuous modes. The concentration of tetrafluoroethylene can be controlled by pressure and/or by dilution with an inert gas such as nitrogen or argon.

The products of this invention are perfluorocarbon chains with terminal carboxylic acid groups,
Oligomers formed by the method of the present invention, wherein $n = 1$ to about 9, are water soluble and were found to be crystalline solids melting over a range from about 35°C to about 70°C. As used herein, the term “water soluble” conveniently denotes those oligomers wherein $n = 1$ to about 9. Of course, as one skilled in the art would appreciate, the $n = 10$ oligomer as well as those oligomers wherein $n$ is greater than 10 are partially soluble in water. Infrared spectra of cold-pressed thin films of the perfluorodiacboxylic acid oligomers show intense absorption bands for carboxylic acid functionality [3500–2500 cm$^{-1}$ (OH) and 1750 cm$^{-1}$ (C = O)], as well as characteristic bands for perfluoroalkyl groups. The mixture of perfluorodiacboxylic acids from a representative reaction was found to have a neutralization equivalent to about 170 g/eq, hence, a molecular weight of about 340 g/m. The products of the methods of the present invention are not monofunctional as evidenced by the fact that all known monofunctional perfluorodiacboxylic acids possessing molecular weights less than 384 g/m are liquids at 20°C.

A portion of the water soluble perfluorodiacboxylic acid mixture was converted to the corresponding anhydride mixture, the anhydride mixture was then hydrolysed to the corresponding acid mixture and the acid mixture was converted to a mixture of methyl diesters. Methyl esters derived from the anhydride mixture were examined by mass spectroscopy and gas chromatography and components of the mixture proved to be identical to known samples, thus confirming the structures of the perfluorodiacboxylic acids. The water soluble perfluorodiacboxylic acid mixture was further characterized by gas chromatography and mass spectroscopy of the methyl diesters. Fractions wherein $n = 2$ and 3 were compared with methyl diesters of authentic perfluorosuccinic and perfluoroglutaric acids and were found to be identical.

The portion of the reaction product which did not dissolve in water (hereinafter referred to as “water insoluble polymer”), was found to contain perfluorodiacboxylic acids wherein $n$ is 10 or greater. Again, as one skilled in the art will appreciate, the “insoluble oligomer” also contained small amounts of what was previously denominated “water soluble”, namely perfluorodiacboxylic acids wherein $n$ is less than 10. The infrared spectrum of a cold-pressed thin film of the water insoluble oligomer showed intense absorption bands, for carboxylic acid functionality [3500–2500 cm$^{-1}$ (OH) and 1700 cm$^{-1}$ (C = O)]. In a mixture of oligomeric diacids prepared from runs having high concentrations of iron or copper promoters the infrared spectrum shows some carbonylate anion [1675 cm$^{-1}$ (C = O)] and the polymer possesses a red or blue discoloration.

Treatment of the water insoluble oligomeric mixture of perfluorodiacboxylic acids with diazomethane in ether permits the isolation of the product as a mixture of methyl diesters. The methyl diesters were analyzed by gas chromatography and mass spectroscopy techniques.

Mass spectral studies of methyl diesters from both water soluble and water insoluble oligomers gave ions in accordance with the homologous series structures. Unzipping of these ions by mass units of 100 ($\text{CF}_2\text{O}$) and 50 ($\text{CF}_3\text{O}$) was frequently observed.

Stepwise oligomerization of tetrafluoroethylene would normally be expected to generate only even-numbered carbon chains, and this is indeed the major reaction pathway because the dominant species found in the product is HOOC($\text{CF}_2\text{O}$)$_n$COOH, wherein $n$ is an even number. However, odd-numbered oligomers are produced via a secondary reaction, namely, oxidative decarboxylation. The oxidative decarboxylation was demonstrated using perfluorodiacboxylic acid as a representative compound.

Treatment of pure perfluoroglutaric acid with aqueous peroxodisulfate in the presence of ferrous ion formed predominantly perfluorosuccinic acid. A second oxidative decarboxylation forms some perfluoromalonic acid. The methods of the present invention and the compositions formed thereby are demonstrated by the following examples.

Example 1

The compositions of the present invention may be prepared by the following method. A solution of potassium peroxodisulfate (5.4 g) in 100 ml of distilled water was placed in an autoclave, with a total capacity of about 300 ml. Ferrous sulfate (200 mg) was placed in the autoclave, having been previously sealed in a fragile glass ampule which would rupture when the solution was stirred. The autoclave was then chilled in dry ice and alternatively evacuated and repirurized with argon in order to deaerate the system. After heating the solution in the autoclave to about 65°C, the argon pressure was adjusted to about 6.4 × 10$^8$Pa (10 psig), a stirrer was activated, and the ampule was broken. Tetrafluoroethylene was introduced to bring the total pressure of the system to about 2.76 × 10$^8$Pa (40 psig). During a period of about 120 minutes, the tetrafluoroethylene pressure was repeatedly adjusted to maintain the total pressure of the system between about 2.62 × 10$^8$Pa (38 psig) and about 2.76 × 10$^8$Pa (40 psig). Upon completion of the reaction, the autoclave was vented, and its contents were filtered through a sintered glass funnel. The autoclave was rinsed and the washings were filtered in order to recover the mixture of water insoluble perfluorodiacboxylic acid oligomers (about 1.1 g). The combined filtrates were treated with potassium iodide to destroy the unreacted peroxodisulfate. The combined filtrates were then distilled to remove iodine. After distillation the concentrate was extracted with ether, and the ether was removed. Solid
crystalline oligomeric perfluorodiacarboxylic acids (1.2 g) were obtained which melted in the range from about 35°C to about 48°C.

The results for this Example are tabulated below in Table I, entry 3. The results for other experiments which illustrate typical reactions of tetrafluoroethylene with aqueous peroxydisulfate are also tabulated below. In all tabulated cases, unless indicated otherwise, the oligomerization was performed with an argon diluent (10 psig) and 100 ml of water, containing K₂S₂O₈ (5.4 g).

**TABLE I**

<table>
<thead>
<tr>
<th>Entry</th>
<th>CF₃ = CF₃ (psig)</th>
<th>Additive</th>
<th>Temp. (°C)</th>
<th>Time (min)</th>
<th>Product Weight (g)</th>
<th>Peroxydisulfate Consumed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40—50</td>
<td>FeSO₄⁺</td>
<td>20—25</td>
<td>100</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>28—30</td>
<td>FeSO₄⁺</td>
<td>60—70</td>
<td>180</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>38—40</td>
<td>FeSO₄⁺</td>
<td>65—75</td>
<td>120</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>4</td>
<td>44—51</td>
<td>CuSO₄⁺</td>
<td>80—90</td>
<td>80</td>
<td>1.9</td>
<td>1.6</td>
</tr>
</tbody>
</table>

* Water Soluble oligomer.  b Water Insoluble oligomer.  c Based on iodometry.  d No Ar diluent, 2.7 g K₂S₂O₈ and 57 mg FeSO₄—7H₂O.  e 0.20 g FeSO₄—7H₂O.  f 40 mg CuSO₄ and 0.47 g copper powder with 8.1 g K₂S₂O₈.

The water soluble fraction of the reaction product mixture was converted with a solution of diazomethane in ether to a mixture of methyl diesters, analysed by gas chromatography, and the relative area percent compositions of the components are tabulated below in Table II.

**TABLE II**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1</td>
<td>1.6</td>
</tr>
<tr>
<td>n = 2</td>
<td>30.3</td>
</tr>
<tr>
<td>n = 3</td>
<td>5.1</td>
</tr>
<tr>
<td>n = 4</td>
<td>28.4</td>
</tr>
<tr>
<td>n = 5</td>
<td>2.2</td>
</tr>
<tr>
<td>n = 6</td>
<td>13.3</td>
</tr>
<tr>
<td>n = 7</td>
<td>1.3</td>
</tr>
<tr>
<td>n = 8</td>
<td>12.2</td>
</tr>
<tr>
<td>n = 9</td>
<td>0.6</td>
</tr>
<tr>
<td>n = 10</td>
<td>3.8</td>
</tr>
<tr>
<td>n = 11</td>
<td>0.3</td>
</tr>
<tr>
<td>n above 11</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Example II

Potassium peroxydisulfate (8.1 g), 100 ml of water, and a promoter of 40 mg of copper powder sealed in a fragile glass ampule were placed in an autoclave. The autoclave was heated to between about 80°C and about 90°C, and the autoclave was deaerated as described in Example I. The solution was stirred and the system was pressurized with argon [6.3 × 10⁷Pa (10 psig)] and tetrafluoroethylene [30.4—35.2 × 10⁷Pa (44—51 psig)] for about 2 hours. Water insoluble (1.9 g) and water soluble (1.8 g) oligomeric perfluorodiacarboxylic acids were obtained after the reaction was worked-up in the manner described in Example I. A cold-pressed film of the oligomeric mixture had a blue discoloration even after the mixture had been extensively washed with water. The results for Example II are tabulated in Table I, entry 4.
Example III

The oxidative decarboxylation of perfluoroglutaric acids is demonstrated as follows. Perfluoroglutaric acid (1.2 g) was dissolved in 25 ml of deionized water containing K₂S₂O₈ (1.35 g). The solution was heated to about 80°C, stirred, and FeSO₄₅H₂O (28 mg) added. Iodometric titrations of aliquots taken after 1 and 2 hours showed that 64% and 81%, respectively, of the peroxysulphate reacted. After 2 hours, a 2 g sample of the solution was treated with an ethereal solution of diazomethane. Gas chromatographic analysis of the methyl diesters indicated that about 32% of the perfluoroglutaric acid was converted to a mixture of perfluorosuccinic acid (57%), and perfluoromalonic acid (14%).

Claims

1. A method for producing a polymeric α,ω-perfluorocarboxylic acid of even- or odd-numbered chain length, of the general formula HOOC(CF₂)ₙCOOH, wherein n is an integer in the range from 1 to 1000, which method comprises the step of:
   reacting tetrafluoroethylene with at least 0.5% by weight of peroxydisulphate salt in an aqueous environment.

2. A method for the oxidative decarboxylation of a starting perfluorocarboxylic acid polymer to produce a perfluorocarboxylic acid polymer having fewer carbon atoms than the starting perfluorocarboxylic acid polymer, which method comprises the step of:
   reacting the starting perfluorocarboxylic acid polymer with at least 0.5% by weight of a peroxydisulphate salt in an aqueous environment.

3. A method according to Claim 1 or 2, wherein a metal ion promoter is used to assist peroxydisulphate decomposition.

4. A method according to any preceding claim, carried out in the temperature range from 35°C to 100°C.

5. A method for producing a composition comprising a water-soluble homologous series of perfluorocarboxylic acids of the general formula HOOC(CF₂)ₙCOOH, wherein n is an integer of from 1 to 9, which comprises:
   (i) reacting tetrafluoroethylene with at least 0.5% by weight of a peroxydisulphate salt in an aqueous environment;
   (ii) separating the aqueous fraction from the non-aqueous fraction; and
   (iii) isolating from the aqueous fraction a composition comprising the said water-soluble homologous series.

6. A method according to Claim 5, wherein the said composition comprising a water-soluble homologous series has a neutralisation equivalent of from 95 to 200 g/ equivalent.

7. A method for producing a water-insoluble homologous series of perfluorocarboxylic acid polymers of the general formula HOOC(CF₂)ₙCOOH, wherein n is an integer in a range from 10 to 1000, which comprises:
   (i) reacting tetrafluoroethylene with at least 0.5% by weight of a peroxydisulphate salt in an aqueous environment;
   (ii) separating the non-aqueous fraction from the aqueous fraction; and
   (iii) isolating from the non-aqueous fraction a composition comprising the said water-insoluble homologous series of perfluorocarboxylic acids.

Patentansprüche

1. Verfahren zur Herstellung einer polymeren α,ω-Perfluoricarbon säure mit gerad- oder ungeradzähliger Kettenlänge und mit der allgemeinen Formel HOOC(CF₂)ₙCOOH, wobei n eine ganze Zahl im Bereich von 1 bis 1000 ist, wobei das Verfahren den Schritt einer Behandlung von Tetrafluorethylen mit wenigstens 0,5 Gewichts-% eines Peroxydisulfatsalzes in wässriger Umgebung umfaßt.

2. Verfahren zur oxidativen Decarboxylierung eines Ausgangs-Perfluoricarbon säure-Polymeren mit weniger Kohlenstoffatomen als das Ausgangs-Perfluoricarbon säure-Polymeren, wobei das Verfahren den Schritt einer Behandlung des Ausgangs-Perfluoricarbon säure-Polymeren mit wenigstens 0,5 Gewichts-% eines Peroxydisulfatsalzes in wässriger Umgebung umfaßt.

3. Verfahren gemäß Anspruch 1 oder 2, bei dem ein Metallionen-Beschleuniger zur Unterstützung der Peroxydisulfat-Zersetzung verwendet wird.

4. Verfahren gemäß einem der vorangegangenen Ansprüche, bei dem die Behandlung in einem Temperaturbereich von 35 bis 100°C erfolgt.

5. Verfahren zur Herstellung einer Zusammensetzung, die eine wasserlösliche homologe Reihe von Perfluoricarbon säuren mit der allgemeinen Formel HOOC(CF₂)ₙCOOH enthält, wobei n eine ganze Zahl von 1 bis 9 ist, wobei
   (i) Tetrafluorethylen in wässriger Umgebung mit wenigstens 0,5 Gewichts-% eines Peroxydisulfatsalzes behandelt wird,
   (ii) die wässerige Fraktion von der nicht wässerigen Fraktion abgetrennt wird und
aus der wässerigen Fraktion eine diese wasserlösliche homologe Reihe enthaltende Zusammensetzung isoliert wird.

6. Verfahren gemäß Anspruch 5, bei dem diese Zusammensetzung mit der wasserlöslichen homologen Reihe ein Neutralisationsäquivalent von 95 bis 200 g/Äquivalent hat.

7. Verfahren zur Herstellung einer wasserunlöslichen homologen Reihe von Perfluorcarbonsäure-Polymeren mit der allgemeinen Formel HOCOCF₃ₙCOOH, wobei n eine ganze Zahl von 10 bis 1000 ist, wobei
   (1) Tetrfluorethyl in wässriger Umgebung mit wenigstens 0,5 Gewichts-% eines Peroxydisulfatsalzes behandelt wird,
   (ii) die nicht wässerige Fraktion von der wässerigen Fraktion abgetrennt wird und
   (iii) aus der nicht wässerigen Fraktion eine diese wasserunlösliche homologe Reihe von Perfluorcarbonsäuren enthaltende Zusammensetzung abgetrennt wird.

Revidications

15. Procédé pour la préparation d’un acide &alpha;&alpha;-perfluorodicarboxylique polymère à longueur de chaîne paire ou impaire, de formule générale HOCOCF₃ₙCOOH, n étant un nombre entier allant de 1 à 1000, lequel procédé comprend l’étape de la réaction du tétrafluoro-éthylène avec au moins 0,5% en poids d’un peroxydisulfate dans un milieu aqueux.

20. Procédé pour la décarboxylation oxydante d’un polymère acide perfluorodicarboxylique initial afin d’obtenir un polymère acide perfluorodicarboxylique ayant moins d’atomes de carbone que le polymère acide perfluorodicarboxylique initial, lequel procédé comprend l’étape de la réaction du polymère acide perfluorodicarboxylique initial avec au moins 0,5% en poids d’un peroxydisulfate dans un milieu aqueux.

25. Procédé selon la revendication 1 ou 2, dans lequel on utilise un promoteur de type ion métallique pour faciliter la décomposition du peroxydisulfate.

30. Procédé selon l’une quelconque des revendications précédentes, effectué à une température allant de 35 à 100°C.

50. Procédé pour la préparation d’une composition comprenant une série homologue soluble dans l’eau d’acides perfluorodicarboxylique de formule générale HOCOCF₃ₙCOOH, n étant un nombre entier allant de 1 à 9, qui comprend:
   (I) la réaction du tétrafluoro-éthylène avec au moins 0,5% en poids d’un peroxydisulfate dans un milieu aqueux;
   (II) la séparation de la fraction aqueuse d’avec la fraction non aqueuse; et
   (III) l’isolement à partir de la fraction aqueuse d’une composition comprenant ladite série homologue soluble dans l’eau.

60. Procédé selon la revendication 5, dans lequel ladite composition comprenant une série homologue soluble dans l’eau a un équivalent de neutralisation allant de 95 à 200 g/équivalent.

70. Procédé pour la préparation d’une série homologue insoluble dans l’eau de polymères acides perfluorodicarboxylique formule générale HOCOCF₃ₙCOOH, n étant un nombre entier allant de 10 à 1000, qui comprend:
   (I) la réaction du tétrafluoro-éthylène avec au moins 0,5% en poids d’un peroxydisulfate dans un milieu aqueux,
   (II) la séparation de la fraction non aqueuse d’avec la fraction aqueuse; et
   (III) l’isolement à partir de la fraction non aqueuse d’une composition comprenant ladite série homologue d’acides perfluorodicarboxyliques, insoluble dans l’eau.