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(54) Title: POLYMERIZATION OF HEXAFLUOROPROPYLENE OXIDE

(57) Abstract: The present invention provides a process for oligomerization of hexafluoropropylene oxide, the process comprising polymerizing a mixture of hexafluoropropylene oxide and hexafluoropropene in the presence of an aprotic organic solvent using KF as a catalyst.



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POLYMERIZATION OF HEXAFLUOROPROPYLENE OXIDE

Cross-Reference to Related Patent Application

This U.S. Patent application claims priority to European Patent Application serial
5 number 05101610.3, filed on March 2, 2005, herein incorporated by reference in its
entirety.

Field of the invention

The present invention relates to the polymerization of hexafluoropropylene oxide
10 (HFPO). In particular, the present invention relates to a polymerization of HFPO that
yields a desired degree of polymerization combined with a low amount of low molecular
weight oligomers of HFPO.

Background

15 Polymerization or oligomerization of HFPO leads to perfluoropolyethers that have
found utility in a wide variety of applications. For example, the resulting
perfluoropolyethers can be used in the manufacturing of surfactants or may be used to
prepare fluorochemical compounds suitable for the treatment of various substrates so as to
render these oil- and/or water repellent. Usually, optimal results in these applications
20 require a fairly low degree of polymerization, i.e. oligomers of HFPO. From an
environmental point of view, such low molecular weight products of HFPO, e.g. having a
degree of polymerization of only 2 to 4 HFPO molecules are not desired.

But, it has been found difficult to prepare HFPO oligomers with a low degree of
polymerization combined with a low or minimal amount of oligomers having a degree of
25 polymerization of 4 or less. Furthermore, it would be desirable to find a robust
polymerization process in which the degree of polymerization and amount of oligomers
with a low degree of polymerization does not vary too much with the polymerization
conditions and in particular is moderate by dependent or independent on the amount of
hexafluoropropylene oxide and polymerization catalyst used.

30 The polymerization of HFPO is well known in the art and has been described in a
variety of publications. US 6,127,517 describes the polymerization of HFPO in the

presence of hexafluoropropylene (HFP) using CsF as a catalyst. In J. Macromol. Sci. Chem., A8 (3), 499-520 (1974) it has been disclosed that HFP prevents chain transfer during the oligomerization of HFPO. DE 2026686 also discloses polymerization of HFPO in the presence of HFP. As a catalyst, active carbon and CsF are used in the examples.

5 GB 1 292 268 discloses silver nitrate as a catalyst for the polymerization of HFPO to produce predominantly dimmers of HFPO.

Summary

The present invention provides a process for oligomerization of
10 hexafluoropropylene oxide, the process comprising polymerizing a mixture of hexafluoropropylene oxide and hexafluoropropene in the presence of an aprotic organic solvent using KF as a catalyst.

It has been found that the above process generally yields only a low amount of HFPO oligomers having a degree of polymerization of less than 5. It has further been
15 found that generally, the degree of polymerization and molecular weight distribution shows little variation with changes in the weight ratio of catalyst to HFPO. In a typical embodiment, the process can provide oligomers having a degree of polymerization of 6 to 10 with the amount of oligomers having a degree of polymerization of 4 or less being low, e.g. not more than 10% by weight, preferably not more than 5% by weight of the total
20 weight of HFPO oligomers produced. Generally, the polymerization process can be carried out in a convenient, easy and cost effective way, yielding the desired HFPO oligomers in an economically effective way. Usually, the production of HFPO results in HFP/HFPO mixtures from which HFP needs to be separated, which is a costly process. The polymerization of HFPO according to the invention can use the crude mixture of
25 HFP/HFPO without separation of the HFP.

Detailed Description

The polymerization of HFPO according to the present invention is carried out using a mixture of HFPO and HFP. While the amount of HFP may vary widely, the molar ratio
30 of HFP to HFPO is typically between 4 and 0.05. In one embodiment, the molar ration

may be between 3 and 0.2. In another embodiment, the molar ratio could be between 2 and 0.25.

The polymerization of HFPO is started using KF as a catalyst. The KF catalyst is typically dissolved or dispersed in an aprotic polar organic solvent. Suitable solvents that can be used include crown ethers and glymes such as monoglyme, diglyme, triglyme and tetraflyme. Further suitable solvents include tetrahydrofuran and 1,4-dioxane. A mixture of solvents can be used as well. Generally, the solvents used in the polymerization should be dried. Typically, the solvents can be dried to a residual water content of not more than 500 ppm. In one embodiment the residual water content of a solvent used could be less than 200 ppm or less than 100 ppm. Solvents with even lower residual water content of for example less than 50 ppm may be used as well.

The use of KF fluoride as a catalyst in the process according to the present invention can provide the advantage that the average degree of polymerization and molecular weight distribution is less dependent on the amount of catalyst used relative to the amount of HFPO fed to the polymerization. Accordingly, varying amounts of HFPO may be fed to the polymerization using a same amount of catalyst without substantially affecting the molecular weight and distribution of the corresponding oligomers produced. Generally, the weight percentage of KF catalyst is between 20 and 0.1 based on the amount of HFPO fed to the polymerization. In one embodiment, the weight percentage of KF catalyst is between 15 and 0.3. In another embodiment, the weight percentage of KF catalyst is between 10 and 0.5.

The polymerization of HFPO is typically carried out at a temperature of -30°C to 50°C. According to a particular embodiment, the polymerization temperature can be between -10 and 20°C. Oligomers having an average polymerization degree of 6 to 10 while yielding low amounts of oligomers having a polymerization degree of less than 5 can typically be produced at a polymerization temperature between -10 and 10°C. It will generally be beneficial to maintain the polymerization temperature constant during polymerization, e.g. within +/- 5°C.

The reaction time is generally not critical and typically, the polymerization will be conducted for a time sufficient to convert most or all of the HFPO into oligomers. Depending on the polymerization temperature used and amount of HFPO to be converted,

the reaction time may vary between 10 minutes and 3 hours. In a typical embodiment, the reaction time is between ½ hour and 1 hour.

The polymerization or oligomerization is typically carried out in a stainless steel vessel. The catalyst solution is typically added to the stainless steel vessel, which may then be brought under a vacuum. The mixture of HFPO and HFP is typically supplied to the vessel as a gas mixture. Once the feed of this gas mixture is complete, the reaction is generally continued until most or all of the HFPO is converted.

The following examples further illustrated the invention.

Examples

The following general polymerization procedure was used in each of the examples: A stainless steel pressure vessel equipped with an effective stirrer and a baffle was used. The internal temperature was controlled by a heating-cooling jacket. A thermocouple in the reaction mixture served as reference for automatic temperature control. The dry reactor was filled with the catalyst consisting of dry KF and diglyme, inerted with dry nitrogen, and set under vacuum (450 to 500 hPa absolute). The mixer was started, the internal temperature was adjusted to the desired temperature, and the HFPO/HFP (1 to 1 by weight) feed was started. After the planned amount of the gas mixture was fed to the reactor, the feed line was closed and the batch was allowed to react at the preset temperature. Gas samples were taken on a regular basis to control the conversion. After conversion of most of the HFPO, the remaining HFP was evaporated. The batch was allowed to reach 20°C, the mixer was stopped and the lower phase was separated. A sample of the lower phase was converted to the methyl ester and analyzed by gas chromatography.

The following describes the input and process variables for each example:

Example 1

Catalyst:	11.6 g KF and 501 g diglyme
Reaction temperature:	0°C
HFPO/HFP fed to reactor:	596 g
Amount of lower phase:	266 g

Example 2

Catalyst: 11.6 g KF and 501 g diglyme

Reaction temperature: 0°C

5 HFPO/HFP fed to reactor: 1100 g

Amount of lower phase: 563 g

Example 3

Catalyst: 11.6 g KF and 501 g diglyme

10 Reaction temperature: 0°C

HFPO/HFP fed to reactor: 2100 g

Amount of lower phase: 1057 g

The following table describes the results:

15 Composition of lower phase (GC results, area %):

	Analytical composition*							
	(HFP)2	(HFP)3	(HFPO)5	(HFPO)6	(HFPO)7	(HFPO)8	(HFPO)9	(HFPO)10
Example 1	7	2.7	0.8	2.5	14.9	43.3	22.6	3.2
Example 2	4.4	3.6	1.2	5.4	23.4	38.5	18	3.4
Example 3	5.6	1.1	2.1	6.4	18.3	34.6	23.4	5.4

*there were no HFPO oligomers in which $n < 5$ detected in the resulting composition.

What is claimed is:

1. Process for oligomerization of hexafluoropropylene oxide, said process comprising polymerizing a mixture of hexafluoropropylene oxide and hexafluoropropene in the presence of an aprotic organic solvent using KF as a catalyst.

5

2. Process according to claim 1 wherein the oligomerization is carried out at a temperature between -10°C and 10°C.

3. Process according to claim 1 wherein the molar ratio of
10 hexafluoropropylene oxide to hexafluoropropylene is between 4 and 0.05.

4. Process according to claim 1 wherein the aprotic solvent is selected from glymes, tetrahydrofuran and 1,4-dioxane.

15 5. Process according to claim 1 wherein the amount of KF is between 20 and 0.1% by weight based on the weight of hexafluoropropylene oxide fed to the polymerization.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2006/006881

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G65/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 033 574 A (E. I. DU PONT DE NEMOURS AND COMPANY) 22 June 1966 (1966-06-22) claim 5; example 2 HFPO contains residual non-oxidized HFP (see DE 20 26 686 p. 1 l. 11-15)	1-5
X	EP 0 834 526 A (SHIN-ETSU CHEMICAL CO., LTD) 8 April 1998 (1998-04-08) claim 5 together with p. 3 l. 31	1-5
X	DE 20 26 686 A1 (VEB CHEMIEKOMBINAT BITTERFELD, X 4400 BITTERFELD) 14 January 1971 (1971-01-14) claim 1 together with p. 4 l. 1 example 3	1-5
X	US 3 382 622 A (DUNN ELMAN R) 14 May 1968 (1968-05-14) claim 5; example 2	1-5



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1033574	A	22-06-1966	DE 1520527 A1	22-05-1969
			DE 1645115 B1	18-11-1971
			DE 1645114 B1	31-05-1972
EP 0834526	A	08-04-1998	DE 69706014 D1	13-09-2001
			DE 69706014 T2	18-04-2002
			JP 3314634 B2	12-08-2002
			JP 10101788 A	21-04-1998
			US 5817746 A	06-10-1998
DE 2026686	A1	14-01-1971	CS 168096 B1	28-05-1976
			FR 2052303 A5	09-04-1971
			SU 370782 A3	15-02-1973
US 3382622	A	14-05-1968	CH 443958 A	15-09-1967
			DE 1577396 A1	07-10-1971
			GB 1146828 A	26-03-1969