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METHOD OF POLYMERIZING PERFLUOROBUTADIENE

The object of this invention is to provide a method for polymerizing perfluorobutadiene under mild conditions. The resulting polyperfluorobutadiene is useful as a hard elastomer for seals and the like where good chemical resistance is needed. Further, the material can serve as an intermediate in graft polymerizations and can be cross-linked to provide high molecular weight materials.

The invention comprises the utilization of a peroxide catalyst mixed with the monomer material to cause the desired polymerization. The catalyst and monomer are preferably disposed in a vacuum sealed flask and the polymerization is allowed to proceed at autogenous pressure. The temperatures during polymerization can range from ambient up to 120°C. One catalyst, di-tert-butyl peroxide, yields a low molecular weight material, while another peroxide, bis(trifluoromethyl) peroxide, yields a higher molecular weight product and gives a much greater yield. When utilizing the bis(trifluoromethyl) peroxide, polymerization is aided by subjecting the mixture to ultra-violet light.

Prior to the herein invention, pressures of up to 10,000 atmospheres were required to polymerize perfluorobutadiene. This was both hazardous and costly. Additionally, extensive equipment was required. The herein method provides a much simpler approach, and when utilizing bis(trifluoromethyl) peroxide extremely good yields can be obtained.

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# S P E C I F I C A T I O N

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT, MADELINE S. TOY, a citizen of the United States of America, residing at Fountain Valley in the County of Orange, State of California, has invented a new and useful

METHOD OF POLYMERIZING PERFLUOROBUTADIENE

of which the following is a specification.

## 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 83-568 (72 Stat. 435; 42 USC 2457).

## BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention is in the field of producing polymer materials, more particularly the invention relates to a novel method for producing high yields of polyperfluorobutadiene under mild reaction conditions.

2. Description of the Prior Art:

Prior to the herein invention, perfluorobutadiene and other halogenated olefins have been polymerized. This has been accomplished in the absence of any catalyst utilizing extremely high pressures, exceeding 10,000 atms, or through the use of gamma radiation. Often both of the aforegoing methods were combined. Under such severe reaction conditions, yields in excess of 90% of polyperfluorobutadiene, for example, have been achieved. Additionally, others have utilized various peroxide type catalysts in an attempt to polymerize the fluorinated olefins. However, in order to obtain high yields even utilizing such catalysts, high pressures and temperatures were once again utilized. To date, the polymerization of perfluorobutadiene had not been obtained in high yields under mild reaction conditions. Utilization of such reaction conditions to achieve the polymerization obviously provides for a safer method of manufacture, as well as decreasing the cost of the end material.

## OBJECTS AND SUMMARY OF THE INVENTION

An object of this invention is to provide a method for producing polyperfluorobutadiene under mild reaction conditions.

Another object of this invention is to provide a method of making polyperfluorobutadiene in high quantitative yields.

A further object of this invention is to provide a simplified method for making polyperfluorobutadiene.

The above and other objects of this invention comprise reacting perfluorobutadiene in the presence of a peroxide catalyst selected from the group consisting of bis(trifluoromethyl) peroxide, benzoyl peroxide, and di-tert-butyl peroxide. The perfluorobutadiene and the catalyst are preferably vacuum sealed in a reaction flask and the polymerization is then allowed to proceed at the autogenous pressure developed. Generally, this pressure is about two atmospheres. The prior evacuation of the reaction flask serves to prevent undesirable side reactions. The polymerization will occur at higher pressures than the two atmospheres, such as would result if the flask was not initially evacuated. The polymerization is then allowed to proceed at temperatures ranging from ambient up to 120°C. Generally the reaction is allowed to proceed for several days. The resulting polymer product will often depend upon the particular peroxide catalyst chosen. For example, di-*tert*-butylperoxide yields a lower molecular weight material. Additionally, the percent yield of material will vary according to the catalyst. For example, the best catalyst is bis(trifluoromethyl) peroxide also utilizing ultra-violet light. This gives quantitative yields of polymer product. It is believed the invention will be better understood from the following detailed description and specific examples.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Perfluorobutadiene is a commercially available monomer material. Because it contains only carbon and fluorine atoms it has extreme promise as a potential polymer which is inert and has good low temperature properties. As such, polyperfluorobutadiene would be suitable for use in various space-propulsion applications where strong oxidizers are encountered, as well as low temperatures. Because of the potential desirable properties of polyperfluorobutadiene several methods were investigated in an attempt to obtain the polymer in good yields.

One method which has been described in the prior art involves the use of high pressure. Attempting to achieve such polymerization, perfluorobutadiene was sealed in evacuated copper tubes. In some tubes a catalytic amount of benzoyl peroxide was added. The tubes were subjected to 4000 atmospheres pressure at ambient temperatures for periods ranging from 2 to 16 hours. Poor yields of less than 5% were obtained. Particularly poor yields were encountered in the absence of the catalyst. Another approach attempting to achieve polymerization involved ultraviolet irradiation. Once again, poor yield was obtained. Further, the product did not have a high molecular weight and was soluble in hexafluorobenzene. A final approach utilized gamma irradiation. However, only a soft wax polymer was obtained which was soluble in hexafluorobenzene.

Surprisingly it was found that relatively high yields of polyperfluorobutadiene can be obtained by the utilization of free radical peroxide catalysts, under very mild reaction conditions. The most preferred peroxide found is bis(trifluoromethyl) peroxide. Unlike the other peroxides, this material is miscible in perfluorobutadiene below ambient temperature. It is hypothesized that the miscibility aids in the attainment of such higher yields with this material. Particularly outstanding results are achieved when the perfluorobutadiene containing the bis(trifluoromethyl) peroxide is subjected to ultraviolet irradiation. Bis(trifluoromethyl) peroxide has a boiling point of -37°C. It has been reported that the peroxide forms a predominantly trifluoromethylperoxy radical, $CF_3OO\cdot$, rather than $CF_3O\cdot$ radical at -196° to -170°C under ultraviolet irradiation. However, at ambient temperature the $CF_3O\cdot$ radical is likely to be the only species present in significant concentration. Thus, the first step of chain initiation utilizing this material is the breaking of the relatively weak O-O bond to give $CF_3O\cdot$ radicals in accord with the following reaction:

$$CF_3OOCF_3 \rightleftharpoons 2CF_3O\cdot$$

After the above reaction transpires a chain initiation mechanism then can take place to provide the desired end polymer product. With the bis(trifluoromethyl) peroxide it is preferable to use from 2 to 5 weight percent of the material based on the amount of perfluorobutadiene. At the higher weight percent one obtains a higher yield of polymer in a shorter period of time. However, the polymer thus obtained tends to have a low molecular weight. This material is normally a gas since it boils at -37°C. Thus, it is preferably condensed in a glass bulb and then into the monomer material. As a result, the catalyst and monomer are in a solid state when the flask is sealed. The monomer material perfluorobutadiene also is normally gaseous at ambient conditions. However, when it is sealed in a vacuum cylinder it obtains a liquid state at ambient temperature. In view of the aforegoing, the herein polymerization reaction is carried out in the liquid state by condensing both the bis(trifluoromethyl) peroxide and the perfluorobutadiene into a flask under vacuum, sealing the flask containing contents in solid state, and allowing the reaction to warm up to liquid state in the closed flask and to proceed at autogenous pressure. The temperature during the reaction period is preferably kept at ambient. Additionally, vigorous stirring is preferably maintained during this period. Heating above 75°C tends to change the liquid phase from colorless to yellow, and the solid polymer from white to pale yellow solid. Coloration caused by heating usually indicates side reactions.

The reaction goes to completion generally in a period of several weeks. A simple trial and error method can be utilized to determine the point at which reaction is completed under various reaction conditions and amount of catalyst. This can be simply accomplished by periodically testing the formed product to determine its low molecular weight. As previously indicated, with bis(trifluoromethyl) peroxide, higher yields are obtained when the reaction vessel is subjected to ultraviolet radiation. Thus it is preferred to utilize a transparent reaction vessel made of material such as a quartz pressure bottle. Ultraviolet radiation can be from a source such as a sun lamp ten inches or the like away from the reaction vessel. For example, under such reaction conditions with the ultraviolet light utilized for a 1-month period of reaction, followed by allowing the materials to sit for an additional one month period, 95% yield is obtained.

As indicated, benzoyl peroxide can also be utilized as a catalyst for forming polyperfluorobutadiene under model conditions. However, this material is not miscible with perfluorobutadiene and the yields are not as good as achieved with bis(trifluoromethyl) peroxide. Benzoyl peroxide has in fact been previously utilized as a catalyst to form perfluorobutadiene. However, the reaction conditions were very severe, involving several thousand atmospheres of pressure.

The yields were high. Thus, surprisingly, it was found that under mild reaction conditions benzoyl peroxide would give significant yields on the order of 16 to 25 percent polymer. In utilizing benzoyl peroxide, the material is preferably sealed in a reaction vessel with the monomer and the reaction is thus conducted under autogenous pressure which is about 2 atmospheres. Preferably, the reaction vessel is heated to a temperature of about 60°C for the reaction period. A broader temperature range for the reaction is 10° to 120°C. However, when using benzoyl peroxide, lower yields are obtained at ambient temperature than at 60°C. During the reaction time, the vessel is constantly stirred. The reaction period can vary from three days to several months. Once again, the length of reaction can be determined by periodically checking the product formed to determine the stabilization thereof. Yields as high as 25% can thus be obtained utilizing the benzoyl peroxide.

When using di-tert-butyl peroxide, the procedure is essentially the same as that for benzoyl peroxide. Like benzoyl peroxide, di-tert-butyl peroxide is not miscible with perfluorobutadiene at ambient temperature, but it becomes miscible around 80 - 100°C. As a result, quantitative yields are not obtainable. Further, it has been found that di-tert-butyl peroxide yields a low molecular weight polyperfluorobutadiene. Preferably when utilizing this peroxide, the reaction temperature is increased to 80 to 100°C because of the miscibility of this peroxide with the monomer. A yield as high as 64% of an elastomeric gum is obtainable.

It is believed that the invention will be better understood from the following detailed examples:

## EXAMPLE I

A bulk polymerization was carried out utilizing bis(trifluoromethyl) peroxide as initiator for polymerization of perfluorobutadiene. 52.4 grams of perfluorobutadiene and 4.4 grams of bis(trifluoromethyl) peroxide were condensed into an evacuated Pyrex pressure bottle having a metal cap and valve. The clear homogenous solution in the pressure bottle under an autogenous pressure of about 2 atmospheres was subjected to vigorous stirring under ultraviolet radiation from a conventional sun lamp disposed ten inches away from the bottle. The temperature of the reaction bottle was ambient during the reaction period, which was seven weeks. After completion of the reaction, the unreacted monomer was discharged into another container through the vacuum system after cooling the pressure bottle. The remaining white resin was dried at 50°C under reduced pressure overnight. A yield of 14.1 grams of polyperfluorobutadiene having a melting point of between 138 and 159°C was obtained. The product was not soluble in hexafluorobenzene, molten perfluoronaphthalene dimethyl sulfoxide concentrated sulfuric acid, but was soluble in octafluorotoluene above 85°C.

## EXAMPLE II

The procedure of Example I was repeated, utilizing the same amount of reactants. However, a quartz pressure bottle was utilized to allow for better transmission of the ultraviolet light. Additionally, the polymerization period was reduced to four weeks. The yield reached was 52%. A 95% yield is obtained using the same reaction conditions except the polymerization period is extended to 2 to 3 months without ultraviolet irradiation after the first month.

EXAMPLE III

In this example benzoyl peroxide was utilized as an initiator by placing 1 gram of it in a Pyrex ampoule equipped with a magnetic stirring rod, into which was evacuated and condensed 36.7 grams of perfluorobutadiene. The ampoule was evacuated and sealed. Thus the polymerization was at an autogenous pressure. Reaction mixture was stirred by placing the reaction vessel in an oil bath which was placed on top of a magnetic stirrer and heater controlled at 60°C for two weeks. The unreacted monomer was discharged into another container through the vacuum system after cooling the container. The white resin was dried at 50°C under reduced pressure overnight to give 6.8 grams of polyperfluorobutadiene which was 18.5% conversion. When the aforegoing procedure was repeated with vigorous stirring and an increased polymerization period, a 25% conversion was obtained.

EXAMPLE IV

The same method of polymer preparation as described in Example III was utilized. However, in this example, the initiator was di-tert-butyl peroxide. The polymerization temperature was increased to 115°C. 7.64 grams of the monomer was polymerized in the presence of .10 milliliters of the peroxide. The reaction vessel was maintained at 115°C for two weeks. A conversion to 4.9 grams of elastomeric gum having a melting point of 90 to 92°C and a molecular weight of 1720 or 11 repeating units was obtained. This is equivalent to a 64% conversion.

The polyperfluorobutadiene formed in accord with the method of the invention has good chemical resistance and can be used where a hard elastomer is desirable. Further, the polymer can serve as a prepolymer to form high molecular weight material that has excellent temperature and other properties.