

NOTICE

The invention disclosed in this document resulted from research in aeronautical and space activities performed under programs of the National Aeronautics and Space Administration. The invention is owned by NASA and is therefore available for licensing in accordance with the NASA Patent Licensing Regulation (14 Code of Federal Regulations 1245.200).

To encourage commercial utilization of NASA-owned inventions, it is NASA policy to grant nonexclusive, royalty-free, revocable licenses to any company or individual desiring to use the invention while the patent application is pending in the U.S. Patent Office and within a specified period, presently two years, after issuance of the patent to NASA. If commercial use of the invention does not occur during this period, NASA may grant a limited exclusive, royalty-free license thereby adding an incentive to further encourage commercial development. Any company desiring to make, use, or sell this invention is encouraged to obtain a royalty-free license from NASA.

Address inquiries and all requests for licenses to Assistant General Counsel for Patent Matters, Code GP-1, National Aeronautics and Space Administration, Washington DC 20546.

Inventors: Madeline S. Toy
James M. Newman

NASA Case NPO-10863

Contractor: McDonnell-Douglas Astro-
nautics Co.
Astropower Laboratory

April, 1969

NEW POLYMERS OF PERFLUOROBUTADIENE
AND METHOD OF MANUFACTURE

Polyperfluorobutadiene can be used as a chemical resistant polymer and is further particularly useful as an intermediate to form higher molecular weight materials when it is cross-linked. Prior to the herein invention, conditions for polymerizing perfluorobutadiene were extremely severe and the yields quite poor. The object of this invention is to provide a simple method of such polymerization and greatly increase the yield of product. Further, in the course of development of the novel method of the invention, a new copolymer form of polyperfluorobutadiene was found.

The herein invention comprises polymerization of perfluorobutadiene utilizing diisopropyl peroxydicarbonate as a catalyst for the polymerization. The catalyst is miscible in the perfluorobutadiene monomer. Preferably at least one weight percent of catalyst is utilized. The catalyst and monomer are vacuum sealed in a reaction flask which is maintained at ambient temperature and the reaction is allowed to proceed at autogenous pressure. Reaction periods have been from 24 hours up to several weeks. The yield is a homopolymer, which is in fact a copolymer of perfluoro-1,2- and 1,4-butadiene. This is the first time that such a copolymer form has been identified.

Prior to the herein invention, perfluorobutadiene required extremely high pressures, on the order of 10,000 atmospheres in order to achieve polymerization. This places severe limitations on the equipment utilized as well as greatly increasing the costs and hazards of producing the polymer. The herein method provides a much simpler method for achieving the polymerization. Further, as an additional benefit, it was found that the material was a copolymer of the 1,2- and 1,4-butadienes, thus providing double bonds on side chains that were along the main backbone of the polymer. These double bonds could be readily attacked for graft polymerization and other desirable cross-linking reactions.

Contract No. NAS7-603

Serial No. 848,325

Filing Date August 7, 1969

NASA NPO-10863

Serial No. 848,325
Filing Date August 7, 1969

1
2
3
4
5
6
7
8
9
10
11

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 and JAMES M. NEWMAN,
citizens of the United States of America, residing at Fountain
Valley, County of Orange, State of California, and Tustin,
County of Orange, State of California, respectively, have
invented new and useful

NEW POLYMERS OF PERFLUOROBUTADIENE
AND METHOD OF MANUFACTURE

of which the following is a specification.

ABSTRACT OF THE DISCLOSURE

16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32

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 new polymers and their method of manufacture. More particularly, the invention relates to a new polymer form of perfluorobutadiene and a novel method of making same.

2. Description of the Prior Art:

Prior to the herein invention, perfluorobutadiene had been polymerized by subjecting it to extremely high pressures on

1 the order of 10,000 atm. Though good yields were obtained,
2 it can be readily appreciated that operating at such high
3 pressures placed severe limitations on the equipment utilized,
4 as well as greatly increasing the hazards and costs of
5 producing the polymer. In some instances, catalysts were also
6 utilized. However, the high pressures were still maintained.
7 Additionally, the polyperfluorobutadiene that had been
8 previously made and reported is indicated as being a relatively
9 straight chain with the double bonds of the butadiene in
10 the straight chain. Such double bonds are not often readily
11 available for grafting monomer materials onto such a backbone
12 and thus if one is desirous of such grafting or providing a cross-
13 linked network, such a straight chain of polybutadiene is
14 not particularly desirable.

15 OBJECTS AND SUMMARY OF THE INVENTION

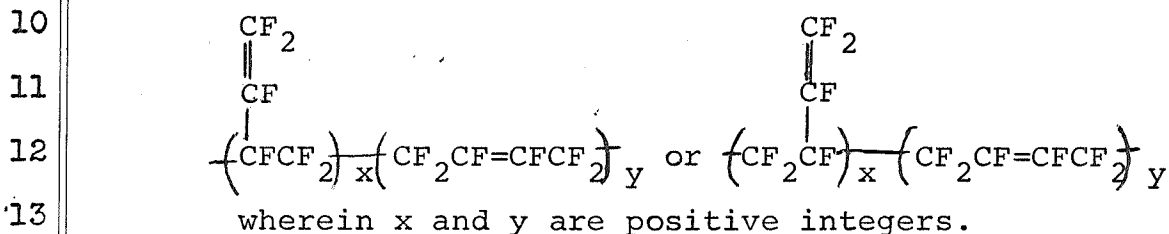
16 An object of this invention is to provide a new method
17 of forming polyperfluorobutadiene under mild reaction conditions.

18 Another object of this invention is to provide a novel
19 copolymer form of polyperfluorobutadiene.

20 Still another object of this invention is to provide
21 a method of obtaining polyperfluorobutadiene in high yield.

22 The above and other objects of this invention are
23 accomplished by initiating the polymerization of polyperfluoro-
24 butadiene with diisopropyl peroxydicarbonate as a catalyst
25 therefor. The peroxydicarbonate is dissolved directly in the
26 liquid polyperfluorobutadiene and the reaction is preferably
27 carried out in a sealed vessel at the autogenous pressure of
28 the polymerization. The degree of the polymerization and the
29 yield of the product depend upon the reaction temperature and
30
31
32

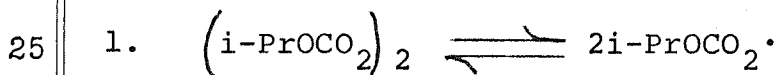
1 the ratio of the catalyst to the monomer. As will be shown,
 2 the yield of polymer will increase with an increasing percent
 3 of catalyst. However, at the higher amount of catalyst the
 4 polymer is of a lower molecular weight. Generally the reaction
 5 temperature is preferably about ambient. Though the material
 6 can be heated, the resulting product will tend to have a
 7 lower molecular weight. Analysis of the resulting polyper-
 8 fluorobutadiene indicates that it is a copolymer of perfluoro-1,2-
 9 and 1,4-butadiene, having the general formulas:



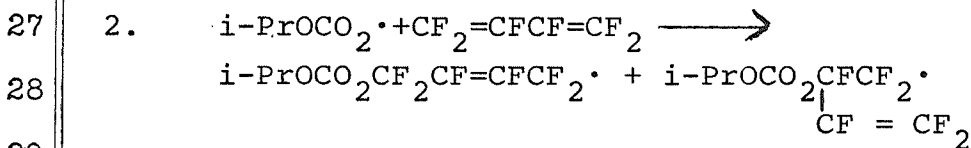
14 It can be seen that the foregoing copolymer has the advantage
 15 of a site change with terminal double bonds which are easily
 16 susceptible to cross linking reactions and graft copolymerizations.

17
18 DESCRIPTION OF THE PREFERRED EMBODIMENTS

19 It is believed that a free radical initiation mechanism
 20 is involved in the polymerization of perfluorobutadiene by
 21 diisopropyl peroxydicarbonate. At relatively low temperatures
 22 diisopropyl peroxydicarbonate is a source of free radicals.
 23 The first step is a homolysis of the oxygen-oxygen bond into iso-
 24 propoxycarboxy radicals in accord with the following reaction:

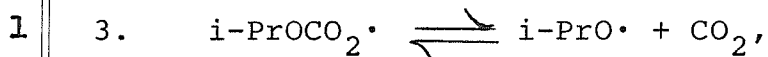


26 after which a chain initiation can occur.



29
30 or a fraction of the radical of equation (1) may undergo
 31 decarboxylation:

32



2 followed by chain initiations.

3 One particular advantage in the utilization of the
4 diisopropyl peroxydicarbonate catalyst is that it is miscible
5 with the perfluorobutadiene monomer. It is believed that this
6 miscibility particularly leads to the attainment of the high
7 yield of polymer product. In carrying out the reaction, the
8 amount of catalyst is not critical. Generally at least 0.10
9 weight percent is required, however, in order to obtain a
10 polymerization. As will be shown, there is a point of catalyst
11 percent where the molecular weight of the end polymer is
12 maximized. Above this percentage of catalyst a decrease in
13 polymer weight is obtained. The reaction is preferably carried
14 out in a pressure bottle which has been chilled by ice bath
15 or the like since the catalyst decomposes at 5°C. Thus, the
16 solid catalyst is placed into the ice-bath chilled pressure
17 vessel which is attached to a vacuum line and evacuated. The
18 chilled and evacuated vessel is then cooled in liquid nitrogen
19 or dry-ice acetone bath and perfluorobutadiene is condensed
20 into the vessel. The bottle is then sealed or closed off from
21 the vacuum line and the materials are continually mixed during
22 the course of reaction. The closed bottle can be heated to about
23 50°C during the reaction period, which can last from 24 hours
24 up to several weeks. Satisfactory results are obtainable,
25 however, at ambient temperature and heating thus is not
26 necessarily required. However, at ambient conditions the
27 yield is somewhat lower. At 50°C the liquid, mostly unreacted
28 monomer, remains colorless and solid polymer remains white.
29 When heated above 50°C, such as 75°C, the liquid turns yellow

30
31
32

1 and the solid polymer turns slightly yellow. The time of
2 reaction required to obtain a product can be determined by
3 a trial and error method for each set of conditions for the
4 polymerization. One merely tests the resultant product at
5 various lengths of time to determine that no further reaction
6 has transpired.

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

9 EXAMPLE I

10 Into an ice chilled 125mm pressure bottle was placed
11 3.4 grams of solid diisopropyl peroxydicarbonate. The pressure
12 bottle was then attached to a vacuum line and evacuated while
13 the bottle was cooling to a liquid nitrogen temperature. The
14 bottle was then charged with 41.7 grams of perfluorobutadiene.
15 Thus, the amount of catalyst was equivalent to 7.4 weight
16 percent. The bottle was then sealed and heated with agitation
17 under autogenous pressure at 50°C for two weeks. White polymer
18 precipitated in the course of the reaction. At the end of
19 the two week period, the pressure bottle was chilled to liquid
20 nitrogen temperature to be opened, then attached to a vacuum
21 line being evacuated, followed by warming to ambient to dis-
22 charge the unreacted monomer under reduced pressure. At
23 ambient temperature, the catalyst decomposes to gaseous products
24 which are easily removed by evacuation. The white homopolymer
25 resulting was then evacuated and dried at 50°C to give 25.2
26 grams of white wax. This is equivalent to a 60% conversion to
27 a polymer. The wax had a melting point between 73 and 76°C
28 and a molecular weight of 1580. The infrared spectrum of the
29 homopolymer showed a copolymer of perfluoro-1,2- and 1,4-butadiene
30
31
32

1 as evidenced by peaks at 5.6 microns indicating the per-
2 fluorovinyl group, (-CF=CF₂), and at 5.8 microns indicating
3 internal -CF=CF- groups.

4 EXAMPLE II

5 The procedure in Example I was repeated except that
6 the amount of catalyst was reduced to 1.9 weight percent,
7 and the polymerization temperature was decreased to ambient.
8 Under these conditions only 16% conversion to a polymer product
9 was obtained. The polymer, however, was a white and hard
10 elastomer having a melting point between 90° and 110°C and
11 molecular weight of at least 7070. The molecular weight of
12 the product could have considerably exceeded the 7070 determined,
13 however the molecular weight was obtained by the Rast method
14 which limits the termination to the 7070 figure. The infrared
15 spectrum of the homopolymer obtained once again indicates
16 copolymer perfluoro-1,2- and 1,4-butadiene.

17 EXAMPLE III

18 The procedure of Example II was repeated. However, the
19 amount of catalyst was increased to 2.7 weight percent. A white
20 hard elastomer was obtained after the two weeks of reaction.
21 The yield was considerably improved, to 31%. The product had
22 a melting point between 80° and 90°C and a molecular weight
23 of 5690. The infrared spectrum indicated a copolymer per-
24 fluoro-1,2- and 1,4-butadiene.

25 Thus it can be seen from the above Examples that the
26 product with the highest molecular weight was obtained with
27 the smallest amount of catalyst. However, a penalty was paid
28 in that the yield was quite low. Alternatively, the product
29 with the highest yield utilized the most catalyst, yet this
30
31
32

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32

product as set forth in Example I was a light wax. The high yield of wax is particularly desirable because the low molecular weight wax is costable at low temperature.

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.