

4

NASA CASE NO. LAR 15020-1

PRINT FIG. N/A

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 patent licensing regulations applicable to U.S. Government-owned inventions (37 CFR 404.1 et seq.).

To encourage commercial utilization of NASA-owned inventions, it is NASA policy to grant licenses to commercial concerns. Although NASA encourages nonexclusive licensing to promote competition and achieve the widest possible utilization, NASA will provide the necessary incentive to the licensee to achieve early practical application of the invention.

Address inquiries and all applications for license(s) for this invention to the Technology Applications Team, NASA Langley Research Center, Code 200, Hampton, Virginia 23681-0001.

Serial No.: 08/299,385
Filed: 09/01/94

LaRC

(NASA-Case-LAR-15020-1) A DIRECT
PROCESS FOR PREPARING
SEMI-CRYSTALLINE POLYIMIDES Patent
Application (NASA Langley
Research Center) 16 p

N95-20407

Unclass

63 127 0039285

P-16
11-27
3-10-95
P-16

AWARDS ABSTRACT

A DIRECT PROCESS FOR PREPARING SEMI-CRYSTALLINE POLYIMIDES

NASA Case Number: LAR 15020-1

Linear aromatic polyimides are typically prepared by reacting a dianhydride with a diamine in the presence of a polar aprotic solvent. The resulting product is a polyamic acid which is subsequently imidized to form a polyimide. Imidization can take place either through chemical dehydration or through the application of heat. The resulting polyimides have exceptional thermal and oxidative stabilities and are useful for such applications as adhesives, matrix resins for composites and molding powders.

By the present invention, a direct process was developed for preparing semi-crystalline polyimides. This process involves reacting a dianhydride and a diamine in the presence of a polar aprotic solvent to form a mixture. Next, glacial acetic acid is added to the mixture at a ratio ranging from 90:10 to 75:25 (polar aprotic solvent : glacial acetic acid) to form a solution. The solution is heated from about 110° to about 140°C to form a polyimide precipitate. The polyimide precipitate is recovered as a semi-crystalline polyimide powder.

The novelty of this invention lies in the addition of glacial acetic acid to the mixture. Glacial acetic acid acts as both a non-solvent and a dehydrating agent in the reaction, thus allowing the polyimide to be formed directly from the dianhydride and the diamine without first forming the polyamic acid. The nonobviousness is found in that when the glacial acetic acid is added at the aforementioned ratios, the polyimides formed by the reaction are semi-crystalline. When the ratio lies in favor of the glacial acetic acid, the polyimides are amorphous.

Inventors: Alice C. Chang
308 Marl Ravine Road
Yorktown, VA 23692
SS: [REDACTED]

Terry L. St. Clair
17 Roberts Landing Drive
Poquoson, VA 23662
SS: [REDACTED]

Employer: Lockheed Eng. & Sci. Co.

NASA LaRC

Initial Evaluator: Darrell R. Tenney

Serial No.: 08/299,385

Filing Date: 9/1/94

A DIRECT PROCESS FOR PREPARING
SEMI-CRYSTALLINE POLYIMIDES

Cross-Reference to Related Applications

5 This application is related to co-pending patent application serial number _____, filed _____, entitled "A Solvent Resistant Copolyimide", and co-pending patent application serial number _____, filed _____, entitled "Copolyimides Prepared from ODPA, BTDA and 3,4'-ODA".

10 Origin of the Invention

 The invention described herein was jointly made by an employee of the United States Government and 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, as amended Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

Background of the Invention

1. Field of the Invention

20 The present invention relates to a process for preparing polyimides. In particular, it relates to a direct process for preparing semi-crystalline polyimides.

2. Description of the Related Art

25 Typically, linear aromatic polyimides are prepared by reacting a dianhydride with a diamine in the presence of a polar aprotic solvent. The resulting product is a polyamic acid which is subsequently imidized to form a polyimide. Imidization can take place either through chemical dehydration or through the application of heat. The resulting polyimides have exceptional thermal and oxidative stabilities and are useful for such applications as
30 adhesives, matrix resins for composites and molding powders.

Despite these properties, many of these polyimides are difficult to process into useful form because of their limited melt-flow properties. Most of the existing polyimides require processing temperatures approaching 400°C and pressures near 10,000 psi in order to sinter to form a well consolidated part. Thus, in order for linear aromatic polyimides to be useful as adhesives, matrix resins and molding powders, it is desired that the polymers exhibit flow at lower temperatures and pressures.

St. Clair (U.S. 5,061,783) sought to achieve this through providing a two-part process for converting the polyamide-acid precursors of polyimides to polyimides which exhibit maximum levels of crystallinity, so that these crystalline forms can then be melted at relatively moderate temperatures to afford adequate flow for molding and consolidation operations. This process involves first dissolving a polyamide-acid in an amide solvent, or a mixture of an ether and an amide solvent, at low percent solids, followed by treating this solution with an aprotic organic base, such as triethylamine or pyridine. The polyamide-acid employed is the reaction product of 3,3',4,4'-benzophenone-tetracarboxylic dianhydride and an aromatic diamine, especially 3,3'-diaminobenzophenone prepared in diglyme, or 4,4'-oxydianiline prepared in dimethyl acetamide, or 3,3'-diaminodiphenylsulfone prepared in diglyme. Finally, this solution is treated with an organic dehydrating agent. St. Clair found that the solubility of the resulting polyimide in the reaction mixture affects the resulting degree of crystallinity. Also, the time that the dehydrated polymer is in contact with the final solution affects the degree of crystallinity.

An object of the present invention is to provide a direct process for preparing semi-crystalline polyimides directly from a mixture of a dianhydride and a diamine.

Another object of the invention is to provide a direct process for preparing semi-crystalline polyimides which may be processed at temperatures just above their melting points.

Another object of the invention is to form finely divided polyimide particles directly from the reaction mixture.

Summary of the Invention

5 By the present invention, the foregoing and additional objects are attained by providing a direct process for preparing semi-crystalline polyimides. This process comprises providing a polar aprotic solvent; adding a dianhydride and a diamine to the solvent to form a mixture; stirring the mixture at ambient temperature; adding glacial acetic acid to the mixture to
10 provide a ratio of polar aprotic solvent to glacial acetic acid which ranges from about 90 to 10 to about 75 to 25 by volume to form a solution. The solution is then heated to a range from about 110° to about 140°C to form a polyimide precipitate. The polyimide precipitate is recovered as a semi-crystalline polyimide powder.

15 In addition to the steps given above, the stoichiometry of the reaction may be offset in order to control the final molecular weight of the polyimide. When there is a molar deficiency in the dianhydride, a monofunctional aromatic anhydride, such as phthalic anhydride, may be added to the mixture or to the solution in order to compensate. Likewise, if there is a molar deficit
20 in the diamine, a monofunctional aromatic amine may be added to the mixture or to the solution to compensate.

Description of the Preferred Embodiments

The process of the present invention requires the use of a polar aprotic
25 solvent. Examples of this solvent include but are not limited to: N-methyl-pyrrolidinone(NMP), N,N-dimethyl acetamide (DMAc) and gamma-butyrolactone (GBL). The preferred solvent is NMP.

A dianhydride and a diamine were added to the solvent to form a mixture. The process will work with any dianhydride but in particular those
30 selected from the group consisting of: isophthaloyldiphthalic anhydride

(IPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-oxydiphthalic anhydride (4,4'-ODPA). The most preferred dianhydride is 4,4'-ODPA. Similarly, any diamine may be employed in the process of the present invention but the preferred diamines include those selected from the group consisting of: m-phenylene diamine (m-PDA), 3,4'-oxydianiline (3,4'-ODA) and 3,3'-diaminodiphenylsulfone (3,3'-DDS). 3,4'-ODA is the most preferred diamine.

The stoichiometry for the mixture may be balanced or offset depending on the final desired molecular weight of the polyimide. By offsetting the stoichiometry, a molar deficit of up to about 5 mole percent may exist for either the dianhydride or the diamine. A molar deficit in the dianhydride was compensated for by adding up to about 10 mole percent of a monofunctional aromatic anhydride (endcapper) to the mixture. In a most preferred embodiment, up to about 10 mole percent of phthalic anhydride (PA endcapper) was added to the mixture to compensate for a molar deficit in the dianhydride. In a like manner, a molar deficit in the diamine is compensated for by adding up to about 10 mole percent of a monofunctional aromatic amine (endcapper) to the mixture. The monofunctional aromatic anhydride or amine may be added to either the mixture (prior to the addition of glacial acetic acid) or the solution (after the addition of glacial acetic acid). When the endcapper was added to the mixture, it was found that the mixture must first be stirred for one hour at ambient temperature prior to adding the endcapper. After the endcapper was added, the mixture had to be stirred for two more hours at ambient temperature prior to the addition of glacial acetic acid.

Glacial acetic acid (GAA) was added to the mixture to form a solution. The ratio of polar aprotic solvent to GAA ranges from about 90 to 10 to about 75 to 25 by volume. When the polyimides were prepared at a ratio of 50 to 50 or with the ratio in favor of the GAA (25 to 75) they were not semi-crystalline, but instead, were amorphous. In a preferred embodiment, the ratio of polar aprotic solvent to GAA is 90 to 10 by volume. In a most

preferred embodiment, NMP is selected as the polar aprotic solvent and GAA is added to provide a ratio of 90 to 10 (NMP to GAA) by volume. It was found that the GAA acts as both a dehydrating agent and as a non-solvent for the formation of the semi-crystalline polyimide.

5 When the stoichiometry was offset and the endcapper was added to the solution (after the addition of the GAA), favorable results were obtained when the solution was stirred for one hour at ambient temperature. After the monofunctional aromatic anhydride or amine was added to the solution, the solution was stirred for two more hours at ambient temperature prior to the
10 application of heat.

 In order for the polyimide to be formed, the solution was heated to a temperature ranging from about 110°C to about 140°C. The addition of heat caused the formation of a polyimide precipitate. The preferred temperature for this reaction is about 120°C. It was observed that at this temperature, the
15 polyimide began to precipitate from the solution after only one hour.

 Once the reaction was complete, the polyimide precipitate was recovered as a semi-crystalline polyimide powder. Any method known to those skilled in the art may be employed in recovering the polyimide powder. An example of one method which was used to recover the polyimide involved
20 collecting the precipitate by filtration, stirring it in hot ethanol for several hours and drying it under vacuum at a temperature of 180°C overnight. Another method involved merely filtering the precipitate from the solution and allowing it to dry at ambient temperature under vacuum.

 The following examples are merely illustrative of the invention and are
25 intended to enable those skilled in the art to practice the invention in all of the embodiments flowing therefrom, and do not in any way limit the scope of the invention as defined by the claims. The results for examples 1 - 12 are summarized in Table 1.

Examples

Example 1

Isophthaloyldiphthalic anhydride (IPDA) (4.9626g, 0.0116 mole, 3 mole
5 percent stoichiometric offset) was added to a stirred solution of m-phenylene
diamine (m-PDA) (1.2978g, 0.012 mole) in a 50/50 (by volume) solvent
mixture comprising NMP (17 ml) and GAA (17 ml) under a nitrogen
atmosphere. The solids content was 15% by weight. The solution was
stirred for one hour at ambient temperature. Phthalic anhydride (PA)
10 (0.1066g, 0.0007 mole, 6 mole percent) was added to the solution and stirring
was continued at ambient temperature for two more hours. The solution was
then heated to 120°C and maintained at that temperature for three hours. It
was observed that the polyimide began to precipitate from the solution after
one hour at 120°C. The precipitated polyimide was collected by filtration,
15 stirred in hot ethanol for two hours, and dried under vacuum at 180°C
overnight. An infrared spectrum showed that the imidization was complete.
The polymer had a glass transition temperature (T_g) of 253.2°C and the x-ray
diffraction pattern showed that the polymer was amorphous.

20

Example 2

The procedure of example 1 was followed to prepare a polyimide from
3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) (3.1257g, 0.0097
mole, 3 mole percent offset) and 3,3'-diaminodiphenylsulfone (DDS)
(2.4830g, 0.01 mole) in a 50/50 (by volume) solvent mixture of NMP (15 ml)
25 and GAA (15 ml). Phthalic anhydride (0.0889g, 0.0006 mole, 6 mole percent)
was added to the solution as an endcapper. The resulting polyimide had a T_g
of 262.3°C. The infrared spectrum showed that the imidization was complete
and the x-ray diffraction pattern showed that the polyimide was amorphous.

30

Example 3

The procedure of example 1 was followed to prepare a polyimide from 4,4'-oxydiphthalic anhydride (ODPA) (3.0092g, 0.0097 mole, 3 mole percent offset) and 3,4'-oxydianiline (3,4'-ODA) (2.0024g, 0.01 mole) in a 50/50 (by volume) solvent mixture of NMP (15 ml) and GAA (15 ml). Phthalic anhydride (0.0889g, 0.0006 mole, 6 mole percent) was added to the solution as an endcapper. The resulting polyimide had a Tg of 209.6°C. The infrared spectrum showed that the imidization was complete and the x-ray diffraction pattern showed that the polyimide was amorphous.

Example 4

The procedure of example 1 was followed to prepare a polyimide from ODPA (3.0092g, 0.0097 mole, 3 mole percent offset) and 3,4'-ODA (2.0024g, 0.01 mole) in a 75/25 (by volume) solvent mixture of NMP (21 ml) and GAA (6.8 ml). Phthalic anhydride (0.0889g, 0.0006 mole, 6 mole percent) was added to the solution as an endcapper. The resulting polyimide had an enthalpy of 38.9 J/g, a melting temperature (Tm) of 290.2°C and a Tg of 231.4°C. The x-ray diffraction pattern showed that the polyimide was semi-crystalline.

Example 5

A polyimide was prepared by adding IPDA (12.7767g, 0.0233 mole, 3 mole percent offset) to a mixture of m-PDA (2.5955g, 0.024 mole) in NMP (53 ml) in the presence of a nitrogen atmosphere. The mixture was stirred at ambient temperature for one hour and phthalic anhydride (0.2559g, 0.00173 mole, 7.2 mole percent) was added. The mixture was stirred for an additional two hours at ambient temperature. GAA (17 ml) was added to the mixture to yield a NMP to GAA ratio of 75 to 25 (by volume) and forming a solution. The solution was heated to 120°C and the temperature was maintained for 10 hours. The polyimide precipitate was filtered from the solution. The resulting

polyimide had a Tg of 248.5°C, a Tm of 299.9°C and an enthalpy of 28.9 J/g. The x-ray diffraction pattern indicated that the polyimide was semi-crystalline and the infrared spectrum showed that the imidization was complete.

5

Example 6

The procedure of example 5 was followed to prepare a polyimide from ODPA (24.0733g, 0.0776 mole, 3 mole percent offset) and 3,4'-ODA (16.0194g, 0.08 mole) in NMP (201 ml). Phthalic anhydride (0.7110g, 0.0048 mole, 6 mole percent) was added to the mixture after it had stirred for one hour at ambient temperature. Stirring at ambient temperature was continued for two more hours after the addition of phthalic anhydride. GAA (22 ml) was added to the mixture to yield a NMP to GAA ratio of 90 to 10 (by volume) and the solution was heated to 120°C and maintained at that temperature for 3 hours. The polyimide was recovered by filtration. The polyimide powder had a Tg of 234.1°C, a Tm of 298.9°C, and a melt viscosity of 6,431 poise at 350°C. The x-ray diffraction pattern indicated that the polyimide was semi-crystalline.

10
15

Example 7

The procedure of example 6 was followed to prepare a polyimide where the stoichiometric offset was 2 mole percent for the ODPA and the phthalic anhydride endcapper was added at 4 mole percent. The ratio of NMP to GAA was maintained at 90 to 10 (by volume). The resulting polyimide had a Tg of 235.7°C and a Tm of 300.5°C. A portion of the polyimide powder was dried at ambient temperature for 10 hours. The x-ray diffraction pattern showed that the polyimide was semi-crystalline.

20

25

Example 8

A polyimide was prepared by adding ODPA (57.081g, 0.184 mole) to a mixture of 3,4'-ODA (40.0484g, 0.2 mole) and NMP (400 ml). The mixture

30

was stirred overnight under nitrogen at ambient temperature. GAA (130 ml) was added to the mixture to provide a NMP to GAA ratio of 75 to 25 (by volume) and the solution was heated to 120°C for three hours. It was observed that the polyimide began to precipitate from the solution after the solution had been heated for two hours. The polyimide powder was recovered from the solution. The resulting polyimide powder had a Tg of 217.6°C, a Tm of 278.4°C and the x-ray diffraction pattern showed that the polyimide was semi-crystalline.

Example 9

The procedure of example 8 was followed to prepare an anhydride terminated polyimide from IPDA (85.2688g, 0.2 mole), m-PDA (20.5474g, 0.19 mole), NMP (436 ml) and GAA (167 ml) (NMP to GAA ratio was 75 to 25 by volume). The reaction time at 120°C was 24 hours. The resulting polyimide had a Tg of 242.9°C and the x-ray diffraction pattern showed that it was semi-crystalline.

Example 10

The procedure of example 4 was followed to prepare the same polyimide but DMAc was substituted for NMP as the solvent. The solvent ratio was 75 to 25 by volume (DMAc to GAA). All other variables and amounts remained the same. The polyimide powder had a Tg of 226.8°C, a Tm of 294.0°C and an enthalpy of 39.4 J/g. The polyimide was semi-crystalline as determined by x-ray diffraction.

Example 11

The procedure of example 7 was followed to prepare the same polyimide but the solvent NMP was replaced with DMAc. The solvent ratio was 90 to 10 by volume (DMAc to GAA). All other variables and amounts remained the same. The polyimide powder had a Tg of 230.8°C, a Tm of

297.8°C and an enthalpy of 33.3 J/g. The polyimide was semi-crystalline as determined by x-ray diffraction.

Example 12

5 The procedure of example 6 was followed to prepare a polyimide having a 3 mole percent stoichiometric offset for the ODPa and 6 mole percent of phthalic anhydride endcapper. The NMP was replaced with gamma-butyrolactone (GBL) to provide a ratio of 90 to 10 by volume (GBL to GAA). The resulting polyimide powder had a T_g of 229.6°C, a T_m of 295.2°C
10 and an enthalpy of 33.2 J/g. The infrared spectrum showed that the imidization was complete and the x-ray diffraction pattern showed that the polyimide was semi-crystalline.

Example 13

15 Neat resin moldings were prepared from the polyimide powder of example 6. Ten grams of the polyimide were placed in a matched metal die mold. The mold was heated to 300°C and maintained for 30 minutes at 0 psi. Next, the mold was pressurized to 1000 psi and the temperature was raised to 330°C where it was held for 1.5 hours. The mold was then cooled to room
20 temperature. The neat resin had a fracture toughness (G_{1c}) of 4956 J/m² at room temperature.

Example 14

25 Neat resin moldings were prepared from the polyimide powder of example 7. Ten grams of the polyimide were placed in a matched metal die mold. The mold was heated to 300°C and maintained for 30 minutes at 0 psi. Next, the mold was pressurized to 1000 psi and the temperature was raised to 330°C where it was held for 1.5 hours. The mold was then cooled to room
30 temperature. The neat resin had a fracture toughness (G_{1c}) of 6860 J/m² at room temperature.

TABLE 1

Example Number	Reaction Conditions	T _m (°C)	T _g (°C)	X-Ray Results
1	50% NMP/50% GAA, 3 mole% IPDA offset, 6 mole% PA endcap	No melt	253.2	Amorphous
2	50% NMP/50% GAA, 3 mole% BTDA offset, 6 mole% PA endcap	No melt	262.3	Amorphous
3	50% NMP/50% GAA, 3 mole% ODPA offset, 6 mole% PA endcap	No melt	209.6	Amorphous
4	75% NMP/25% GAA, 3 mole% ODPA offset, 6 mole% PA endcap	290.6	231.4	Semi-crystalline
5	75% NMP/25% GAA, 3 mole% IPDA offset, 7.2 mole% PA endcap	299.9	248.5	Semi-crystalline

Table 1 continued

Example Number	Reaction Conditions	T _m (°C)	T _g (°C)	X-ray Results
6	90% NMP/10% GAA, 3 mole% ODPA offset, 6 mole% PA endcap	298.9	234.1	Semi-crystalline
7	90% NMP/10% GAA, 2 mole% ODPA offset, 4 mole% PA endcap	300.5	235.7	Semi-crystalline
8	75% NMP/25% GAA, 8 mole% ODPA offset, No endcap	278.4	217.8	Semi-crystalline
9	75% NMP/25% GAA, 8 mole% IPDA offset, No endcap	264.0	242.9	Semi-crystalline

Table 1 continued

Example Number	Reaction Conditions	T _m (°C)	T _g (°C)	X-ray Results
10	75% DMAc/25% GAA, 3 mole% ODPa offset, 6 mole% PA endcap	294.0	226.8	Semi-crystalline
11	90% DMAc/10% GAA, 2 mole% ODPa offset, 4 mole% PA endcap	297.8	230.8	Semi-crystalline
12	90% GBL/10% GAA, 3 mole% ODPa offset, 6 mole% PA endcap	295.2	229.6	Semi-crystalline

A DIRECT PROCESS FOR PREPARING
SEMI-CRYSTALLINE POLYIMIDESAbstract of the Disclosure

5 The invention is a direct process for preparing semi-crystalline polyimides. This process comprises the steps of: providing a polar aprotic solvent, adding a dianhydride and a diamine to the solvent to form a mixture, stirring the mixture at ambient temperature, and adding glacial acetic acid to the mixture to provide a ratio of polar aprotic solvent to glacial acetic acid
10 which ranges from about 90 to 10 to about 75 to 25 by volume to form a solution. The solution was heated to a range from about 110°C to about 140°C to form a polyimide precipitate. The polyimide precipitate was recovered as a semi-crystalline polyimide powder.