Tough, soluble, aromatic, thermoplastic copolyimides were prepared by reacting 4,4'-oxydiphthalic anhydride, 3,4,3',4'-biphenyltetracarboxylic dianhydride and 3,4'-oxydianiline. Alternatively, these copolyimides may be prepared by reacting 4,4'-oxydiphthalic anhydride with 3,4,3',4'-biphenyltetraarboxylic dianhydride and 3,4'-oxydiisocyanate. Also, the copolyimide may be prepared by reacting the corresponding tetra acid and ester precursors of 4,4'-oxydiphthalic anhydride with 3,4,3',4'-biphenyltetraarboxylic dianhydride with 3,4'-oxydianiline. These copolyimides were found to be soluble in common amide solvents such as N,N'-dimethyl acetamide, N-methylpyrrolidinone, and dimethylformamide allowing them to be applied as the fully imidized copolymer and to be used to prepare a wide range of articles.

17 Claims, No Drawings
TOUGH SOLUBLE AROMATIC THERMOPLASTIC COPOLYMIDES

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part application from commonly owned patent application Ser. No. 09/062,082, filed Apr. 17, 1998, now abandoned which is a continuation patent application of Ser. No. 08/359,752, filed Dec. 16, 1994, now U.S. Pat. No. 5,741,883.

ORIGIN OF THE INVENTION

The invention described herein was made by an employee of the United States Government, and may be manufactured and used by or for the Government without payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to copolymides. In particular, it relates to soluble copolymides prepared from 4,4'-oxydiphthalic anhydride, 3,4,3',4'-biphenyltetracarboxylic dianhydride and 3,4'-oxydianiline. It relates also to these same soluble copolymides prepared from 4,4'-oxydiphthalic anhydride, 3,4,3',4'-biphenyltetracarboxylic dianhydride and 3,4'-oxydilisocyanate. It furthermore relates to these copolymides prepared from reacting the corresponding tetra acid and ester precursors to 4,4'-oxydiphthalic anhydride and 3,4,3',4'-biphenyltetracarboxylic dianhydride with 3,4'-oxydianiline.

2. Description of the Related Art

Aromatic, thermoplastic polyimides are a class of polymers used in a variety of high performance/high temperature applications. Such applications include adhesives, matrix resins for composites, and high strength films and coatings. These thermoplastic polyimides are usually soluble in either high boiling polar organic solvents, such as m-cresol and chlorophenol or halogenated solvents such as tetrachloroethylene and multihalogenated aromatics, many of which are highly toxic and are not used in large scale industrial processes without solvent recovery systems. Thus, the majority of polyimide thermoplastics are solution processed in the polyamic acid state using milder solvents and subsequently cyclodehydrated to form the final polyimide article. However, there is a disadvantage to using the polyamic acid intermediates in that they are unstable, susceptible to hydrolysis, and generate water duringimidization.

Attempts to increase the solubility of polyimides generally involve the modification of the polymer backbone through monomer selection. These modifications include the incorporation of flexible aliphatic units, polar and nonpolar pendant substituents, heteroatoms or groups, and polyimide copolymers. These modifications include the incorporation of flexible aliphatic units, polar and nonpolar pendant substituents, heteroatoms or groups, and polyimide copolymers which contain either mixtures of the above monomers with common aromatic diamines and dianhydrides, or block segments of soluble oligomers. Although most of these polyimides meet and even exceed some of the criteria required to find wide spread use as high performance materials, cost limits their acceptance.

By the present invention, wholly aromatic, thermoplastic polyimide copolymers were prepared based on 4,4'-oxydiphthalic anhydride, 3,4,3',4'-biphenyltetracarboxylic dianhydride and 3,4'-oxydianiline. These copolymides were found to be tough thermoplastics which are soluble in common amide solvents such as N,N'-dimethylacetamide (DMAC), N-methylpyrrolidinone (NMP), and dimethylformamide (DMF) and thus can be applied as the fully imidized copolymer in addition to the amic acid solution.

Meterko et al. (U.S. Pat. No. 5,181,028) had prepared copolymides from 4,4'-oxydiphthalic anhydride, 3,4,3',4'-biphenyltetracarboxylic dianhydride and 4,4'-oxydianiline or para-phenylenediamine. The difference between the present invention and that of Meterko et al. lies in the use of 3,4'-oxydianiline as compared to 4,4'-oxydianiline. Meterko et al. prepared polyimide films by pouring the polyamic acid into the desired form. The polyamic acid was then cured either by heating or through chemical imidization. Meterko et al. found that their copolymides had unexpectedly high comparative tracking indexes which made the copolymides useful as insulators for various electronic applications. It is important to note that Meterko et al. applied their copolyimide as a polyamic acid prior to imidizing and not as an imidized solution.

St. Clair et al. (U.S. Pat. No. 5,147,966) prepared polyimide molding powders, coatings, adhesives and matrix resins from 3,4'-oxydianiline and 4,4'-oxydiphthalic anhydride. They found that by preparing polyimides and polyamic acids from these monomers, along with suitable endcaps, adhesives, composite matrix resins, neat resin moldings, and films or coatings had identical or superior properties to commercially available polyimides. Unfortunately, as with Meterko et al., these polyimide homopolymers were applied as the amic acid solution.

Tamai et al. (U.S. Pat. No. 5,268,446) prepared readily melt-processable polyimides by reacting 3,3',4,4'-biphenyltetracarboxylic dianhydride with 3,4'-oxydianiline. They found that these polyimides had excellent processability and chemical resistance in addition to essential heat resistance. These polymers may be used in various fields such as electric and electronic appliances, space and aeronautical equipment and transportation machinery. They note in example 1 that the polyimide was insoluble in halogenated hydrocarbon solvents such as methylene chloride and chloroform. In addition, they prepared films from the amic acid solution instead of from the imide powder.

An object of the present invention is to prepare a tough, soluble, aromatic, thermoplastic copolyimide.

Another object of the invention is to prepare a diverse group of articles from the copolyimide.

SUMMARY OF THE INVENTION

The foregoing and additional objects of the invention were achieved by preparing a tough, soluble, aromatic, thermoplastic copolyimide by reacting 4,4'-oxydiphthalic anhydride with 3,4,3',4'-biphenyltetracarboxylic dianhydride and 3,4'-oxydianiline. Alternatively, the tough, soluble aromatic thermoplastic copolyimide may be prepared by reacting 4,4'-oxydiphthalic anhydride with 3,4,3',4'-biphenyltetracarboxylic dianhydride and 3,4'-oxydilisocyanate. Also, the copolyimide may be prepared by reacting the corresponding tetra acid and ester precursors of 4,4'-oxydiphthalic anhydride and 3,4,3',4'-biphenyltetracarboxylic dianhydride with 3,4'-oxydianiline.

The tough, soluble, aromatic, thermoplastic copolyimide may be used to prepare the following articles: a solvent cast film, an extrudable object, a fiber-reinforced composite, a neat resin molding, a coating, a hot-melt adhesive film, a hot-melt adhesive cloth, a hot-melt adhesive tape, a fiber, a filled resin molding and a matrix composite. The matrix composite further comprises a powder. As a preferred embodiment, this powder is selected from the group con-
consisting of: plastic, metal, graphite and ceramic. The tough, soluble, aromatic thermoplastic copolyimide may furthermore be used as a foam, a tack-free recastable film, and a particulate filled thin film and coating. As a preferred embodiment, this particle is selected from the group consisting of: metals, plastics, ceramics and non-metallics such as carbon and boron and any combination thereof.

The copolyimide of the present invention may be terminated with either a monofunctional anhydride or a monofunctional amine endcapper. The endcapper is added to the copolyimide at an amount ranging from about 2 mole percent to about 10 mole percent. An example of this endcapper is phthalic anhydride. Other endcappers include: maleic anhydride, phenylethynyl anhydride, ethynyl anhydride, nadic anhydride, vinyl anhydride, allylic anhydride, benzocyclobutane anhydride, phenylethynyl amine, ethynylaniline, vinylaniline and allylaniline. These endcapped copolyimides may be used to prepare the articles listed above.

The 4,4'-oxydiphthalic anhydride and the 3,4,3',4'-biphenyltetracarboxylic dianhydride are added to the 3,4'-oxydianiline at a ratio of 25 mole percent to 75 mole percent (25:75) to about 75 mole percent to about 25 mole percent (75:25).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

By the present invention, a copolyimide was prepared by reacting 4,4'-oxydiphthalic anhydride (ODPA) with 3,4,3',4'-biphenyltetracarboxylic dianhydride (BPDA) and 3,4'-oxydianiline (3,4'-ODA). Alternatively, the tough, soluble aromatic thermoplastic copolyimide may be prepared by reacting 4,4'-oxydiphthalic anhydride with 3,4,3',4'-biphenyltetracarboxylic dianhydride and 3,4'-oxydiisocyanate. Also, the copolyimide may be prepared by reacting the corresponding tetra acid and ester precursors of 4,4'-oxydiphthalic anhydride and 3,4,3',4'-biphenyltetracarboxylic dianhydride with 3,4'-oxydiisocyanate. This copolyimide has the following repeat unit:

These copolyimides may be endcapped with either a monofunctional anhydride or a monofunctional amine at an amount ranging from about 2 mole percent to about 10 mole percent. The preferred endcapper is phthalic anhydride. The articles prepared from these copolyimides are the same as those listed above.

In particular, the 4,4'-oxydiphthalic anhydride and the 3,4,3',4'-biphenyltetracarboxylic dianhydride are added to the 3,4'-oxydianiline at a ratio of 50 mole percent 4,4'-oxydiphthalic anhydride to 50 mole percent 3,4,3',4'-biphenyltetracarboxylic dianhydride. An endcapper such as a monofunctional anhydride or a monofunctional amine may also be added to the copolyimide at an amount ranging from about 2 mole percent to about 10 mole percent. Preferably, the endcapper is phthalic anhydride. These copolyimides may be used to prepare the articles which are listed above.

When ODPA and BPDA are used in equal proportion. It has been found to be a tough thermoplastic material. In addition, the copolyimide may be redissolved in common amide solvents such as DMAc, NMP and DMF after the imide powder has been formed, provided that the polyimide is not exposed to temperatures above its glass transition temperature (Tg). (Typically, once a polyamic acid has been converted to the imide, it cannot be redissolved in common
This unique property allows these copolyimides to be used for a large number of applications. For example, films which were cast from the copolyimide after it had been dissolved in solvent and dried above the Tg were found to exhibit high modulus, good chemical resistance and be self-bonding. The self bonding property and insolubility above the Tg allows layered films and coatings to be prepared. These copolyimides can also be extruded which provides them with the capability to form a wide range of objects. Because of their unique combination of properties, fiber-reinforced composites can also be prepared from these copolyimides. Coatings prepared from these copolyimides were successfully used to coat Kapton®, glass, aluminum, copper, ceramic and titanium substrates. It was found that these copolyimides are capable of bonding to themselves as well as many other materials and thus, they are useful as hot-melt adhesive films, hot-melt adhesive cloths and hot-melt adhesive tapes. As yet another application, these copolyimides find utility as neat resin moldings and filled resin moldings, and can be processed at temperatures slightly below the Tg of the copolyimide which can be readily molded and polished. Matrix composites, which can also be produced at temperatures slightly below the Tg of the copolyimide, have been successfully prepared from these copolyimides. These composites were prepared by combining the copolyimide with whiskers and/or a powder. Any powder known to those skilled in the art may be used. Examples of these powders include but are not limited to: graphite, ceramic, metal, plastic, copper, iron, diamond dust, polyimide powder, boron, aluminum, and chopped carbon fibers. More specifically, ceramic powders such as silicon nitride, quartz, zirconia, mixed oxides and aluminum oxide may be used. Plastic powders which may be used include any powder which may withstand the high processing temperature. As a preferred embodiment, the powder may be a plastic, metal, graphite or ceramic powder. Furthermore, these copolyimides find utility as a foam, created from volatile evolution at elevated temperatures. Also, these copolyimides may be used for a tack-free recastable film, created from solvent containing tack-free flexible film. Finally, these copolyimides may find utility as a particulate filled thin film and coating, where the particles can be selected from the group consisting of: metals, plastics, ceramics and non-metals such as carbon and boron and any combination thereof.

The degree of solubility of these copolyimides can be controlled by the processing conditions used to prepare the copolyimide. Several factors were found to affect the solubility of the copolyimide. One of these factors was the mole ratio of ODPA to BPDA. In addition, the percentage of solids and the solvent used to synthesize the copolyimide was also found to have an effect on the solubility. For example, it was observed that when the ratio of ODPA to BPDA was 75 mole percent to 25 mole percent (75:25), and the copolyimide was prepared at 30% solids in NMP, a turbid gel formed when the solution was cooled to room temperature. However, for the same mole ratio, when a 15% solids solution was prepared, the copolyimide remained soluble in NMP when the solution was cooled to room temperature. For a 50:50 mole ratio of ODPA to BPDA copolyimide prepared in NMP, it was found that the copolyimide remained soluble and if allowed to remain undisturbed for 6 to 48 hours (depending on the percent solids) formed a normally and mechanically reversible gel when the copolyimide was prepared using up to 60% solids. When DMAc was substituted as the solvent, the copolyimide was soluble at 15% solids but precipitated out at 30% solids. As with the 75/25 ODPA/BPDA ratio, copolyimides synthesized at a molar ratio of 25/75 ODPA/BPDA were found to remain soluble in NMP at 30% solids during imidization but when cooled to room temperature formed either a turbid gel or an elastomeric homogeneous gel. At 15% solids in NMP, the copolyimides remained soluble. It was also observed that all of the copolyimides remained soluble in m-cresol. In addition to controlling the mole ratio and percent solids, it was found that controlling the molecular weight of the copolyimide affected the sol-gel behavior.

In order to control the molecular weight of these copolyimides, the stoichiometry may be offset and the copolyimide may be terminated with an endcapper such as a mono-functional anhydride or a monofunctional amine. A preferred endcapper is phthalic anhydride. Other endcapers include: maleic anhydride, phenylethynyl anhydride, ethynyl anhydride, nadic anhydride, vinyl anhydride, allylic anhydride, benzocyclobutene anhydride, phenylethynyl amine, ethynylaniline, vinylaniline and allylaniline. The endcapper may be added to the copolyimide at an amount ranging from about 2 mole percent to about 10 mole percent depending on the desired properties of the copolyimide. The addition of the endcapper may allow for better processing in some instances.

As a preferred embodiment of the invention, it was found that good results were obtained when the ODPA and the BPDA were added to the 3,4'-ODA at a ratio of ODPA to BPDA ranging from about 25 mole percent to about 75 mole percent (25:75) to about 75 mole percent to about 25 mole percent (75:25). More preferably, the best results were obtained when the ratio of ODPA to BPDA was 50 mole percent to 75 mole percent (50:75). The addition of an endcapper such as a monofunctional amine or a monofunctional anhydride allowed for molecular weight control which provides versatility in the final end-use of the copolyimides. An alternative method for making the copolyimide allows for the replacement of the diamine with a disocyanate. In the instant case, 3,4-oxydiphenylisocyanate is used in place of 3,4'-oxygen. Thus, the tough, soluble aromatic thermoplastic copolyimide may be prepared by reacting 4,4'-oxydiphthalic anhydride with 3,4,3',4'-biphenyltetra carboxylic diamide and 3,4'-oxydiphenylisocyanate.

Yet another method for making the copolyimide requires the replacement of the diamine with their corresponding tetra acid or ester precursors. This procedure allows for the synthesis of a viscous monomer system, which can be converted, to the polyimide through the application of heat. The advantage is that these acids and esters are the starting materials to afford the corresponding diamidcys. Hence, the additional chemical reactions and purification procedures required to generate the dianhydridnes from the tetra-acids can be avoided. In a similar manner, the conversion to the tetraesters by treating the tetra acids with the required alcohol affords a viscous monomer system, which can be converted, to the polyimide through the application of heat. Thus, the tough, soluble aromatic thermoplastic copolyimide may be prepared by reacting the corresponding tetra acid or ester precursors of 4,4'-oxysthaphalic anhydride and 3,4,3',4'-biphenyltetra carboxylic diamide with 3,4'-oxydianiline.

The following examples illustrate the preparation and use of the copolyimides. These examples are merely illustrative and 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.

**EXAMPLES**

**Example 1**

In a 500 mL resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser...
were placed ODPA (commercially available from Imitec, Inc.) (17.0257 g, 0.0549 mol), BPDA (commercially available from Ube Industries, Inc.) (5.4137 g, 0.0184 mol), 3,4'-ODA (commercially available from Mitsubishi Toatsu Chemical Co.) (15.0231 g, 0.0750 mol), phthalic anhydride (0.4533 g, 0.00306 mol) and NMP (216 g). The solution was stirred overnight at room temperature. Toluene (50 g) was added to the solution and the mixture was heated to 165°C for 7 hours, during which time water was removed by azotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting copolyimide powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 200°C for 9 hours.

Example 2

In a 100 mL resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (15.9407 g, 0.0514 mol), BPDA (5.0395 g, 0.0171 mol), 3,4'-ODA (14.1435 g, 0.0706 mol), phthalic anhydride (0.2877 g, 0.0042 mol) and NMP (81.5 g). The solution was stirred overnight at room temperature. Toluene (20 g) was added to the solution and the mixture was heated to 165°C for 7 hours during which time water was removed by azotropic distillation. The reaction was cooled to room temperature forming a turbid gel. The copolyimide was precipitated in water and chopped with a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 200°C for 9 hours.

Example 3

In a 500 mL resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (16.0239 g, 0.0516 mol), BPDA (15.1975 g, 0.05165 mol), 3,4'-ODA (20.6862 g, 0.1033 mol) and NMP (120 g). The solution was stirred overnight at room temperature forming a heavy gel. Toluene (25 g) was added to the solution and the mixture was heated to 165°C for 7 hours, during which time water was removed by azotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The remaining copolyimide powder was precipitated using water and chopped in a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 200°C for 12 hours.

Example 4

In a 1 L resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap and condenser were placed ODPA (35.8835 g, 0.1156 mol), BPDA (34.0329 g, 0.1156 mol), 3,4'-ODA (46.7922 g, 0.2537 mol), phthalic anhydride (0.0922 g, 0.00467 mol) and NMP (274 g). The solution was stirred overnight at room temperature. Toluene (50 g) was added to the solution and the mixture was heated to 165°C for 7 hours, during which time water was removed by azotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 180°C for 9 hours.

Example 5

In a 1 L resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap and condenser were placed ODPA (213.13 g, 0.6870 mol), BPDA (202.14 g, 0.6870 mol), 3,4'-ODA (200.76 g, 1.4020 mol), phthalic anhydride (8.3072 g, 0.0561 mol) and NMP (1640 g). The solution was stirred overnight at room temperature. Toluene (300 g) was added to the solution and the mixture was heated to 165°C for 7 hours, during which time water was removed by azotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting copolyimide powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 180°C for 9 hours.

Example 6

In a 1 L resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (39.2347 g, 0.1265 mol), BPDA (37.2112 g, 0.1265 mol), 3,4'-ODA (51.6841 g, 0.2581 mol), phthalic anhydride (1.5292 g, 0.0132 mol) and DMAc (740 g). The solution was stirred overnight at room temperature. Toluene (100 g) was added to the solution and the mixture was heated to 165°C for 7 hours during which time water was removed by azotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 200°C for 12 hours.

Example 7

In a 1 L resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (3.6850 g, 0.01246 mol), BPDA (3.6656 g, 0.01246 mol), 3,4'-ODA (5.0922 g, 0.02543 mol), phthalic anhydride (0.1506 g, 0.00102 mol) and m-cresol (38 g). The solution was stirred overnight at room temperature forming a slurry. The mixture was heated to 195°C for 6 hours. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using methanol and chopped in a blender. The resulting copolyimide powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 180°C for 9 hours.

Example 8

In a 1 L resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (38.8358 g, 0.1251 mol), BPDA (36.8329 g, 0.1251 mol), 3,4'-ODA (15.9681 g, 0.2581 mol), phthalic anhydride (2.2939 g, 0.0155 mol) and NMP (303 g). The solution was stirred overnight at room temperature. Toluene (23 g) was added to the solution and the mixture was heated to 165°C for 7 hours during which time water was removed by azotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 200°C for 9 hours.

Example 9

In a 1 L resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser

Example 10

In a 1 L resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (commercially available from Imitec, Inc.) (17.0257 g, 0.0549 mol), BPDA (commercially available from Ube Industries, Inc.) (5.4137 g, 0.0184 mol), 3,4'-ODA (commercially available from Mitsubishi Toatsu Chemical Co.) (15.0231 g, 0.07502 mol), phthalic anhydride (0.4533 g, 0.00306 mol) and NMP (216 g). The solution was stirred overnight at room temperature. Toluene (50 g) was added to the solution and the mixture was heated to 165°C for 7 hours, during which time water was removed by azotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting copolyimide powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 180°C for 9 hours.
were placed ODPA (40.3856 g, 0.1301 mol), BPDA (38.3028 g, 0.1301 mol), 3,4'-ODA (55.4641 g, 0.2769 mol), phthalic anhydride (4.9232 g, 0.03324 mol) and NMP (327 g). The solution was stirred overnight at room temperature. Toluene (35 g) was added to the solution and the mixture was heated to 165° C. for 7 hours during which time water was removed by azeotropic distillation. The solution was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 180° C. for 9 hours.

Example 10
In a 1 L resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (41.1663 g, 0.1327 mol), BPDA (39.0432 g, 0.1327 mol), 3,4'-ODA (55.9411 g, 0.2793 mol), phthalic anhydride (4.1379 g, 0.02794 mol) and NMP (327 g). The solution was stirred overnight at room temperature. Toluene (30 g) was added to the solution and the mixture was heated to 165° C. for 7 hours during which time water was removed by azeotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 180° C. for 9 hours.

Example 11
In a 500 mL resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (5.9869 g, 0.0193 mol), BPDA (17.0345 g, 0.05326 mol), 3,4'-ODA (14.5104 g, 0.07246 mol), phthalic anhydride (1.57326 g, 0.07877 mol), phthalic anhydride (0.4667 g, 0.00315 mol) and NMP (225 g). The solution was stirred overnight at room temperature. Toluene (50 g) was added to the solution and the mixture was heated to 165° C. for 7 hours during which time water was removed by azeotropic distillation. The reaction was cooled to room temperature. The solution was forced through a 5 μm filter. The copolyimide was precipitated using water and chopped in a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 200° C. for 9 hours.

Example 12
In a 100 mL resin kettle equipped with a nitrogen inlet, overhead stirring assembly, Dean-Stark trap, and condenser were placed ODPA (5.5076 g, 0.01775 mol), BPDA (15.6707 g, 0.05326 mol), 3,4'-ODA (14.5104 g, 0.07246 mol), phthalic anhydride (0.4293 g, 0.00292 mol) and NMP (84 g). The solution was stirred overnight at room temperature. Toluene (15 g) was added to the solution and the mixture was heated to 165° C. for 7 hours during which time water was removed by azeotropic distillation. The reaction was cooled to room temperature forming a solid gel. The gel was placed in water and chopped with a blender. The resulting polymer powder (bright yellow in color) was collected by filtration, extracted with methanol for 48 hours and dried in vacuo at 200° C. for 9 hours.

Example 13
Copolyimide films were prepared from polyamic acid solutions using the following procedure. The polyamic acid solutions were doctored onto plate glass and placed in a dust free chamber until they were tack free. The dry polyamic acid films were cured at 100, 200 and 300° C. for 1 hour each in air. The thin films were cut into 0.20 inch strips and the tensile properties were determined at several temperatures. These properties are given in Table 1.

Example 14
A Copolyimide film was prepared directly from the reaction mixture containing BPDA/ODPA (50/50), 3,4'-ODA copolyimide at a 2% offset ratio according to the following procedure. The copolyimide solution was doctored onto plate glass and placed in a dust free chamber until it was tack free. The dry copolyimide film was heated at 100, 200 and 300° C. for 1 hour each in air. The thin film was cut into 0.20 inch strips and the tensile properties were determined at several temperatures. The results are given in Table 2.

Example 15
The following procedure was followed to prepare copolyimide films from the copolyimide powder. Copolyimide powders prepared at 2% offset were dissolved in a NMP/toluene or mixed xylene (9/1 weight) solution over a 12 hour period at 23° C. to form 15% by weight solid solutions. These copolyimide solutions were doctored onto plate glass and placed in a dust free chamber until they were tack free. The dry copolyimide films were heated under several conditions: 100 and 200° C.; 100 and 225° C.; 100, 200, 300° C.; or 100, 225 and 350° C. for 1 hour each in air. The films were removed from the glass plates by soaking in water. The thin films were cut into 0.20 tooth inch strips and the tensile properties were determined at several temperatures. The unoriented thin film properties for the films cured at 100, 200 and 300° C. for 1 hour each in air are listed in Table 3.
at the inflection point in the heat flow vs. temperature curve
and the melting temperature (Tm) taken at the minimum of
the endothermic depression. Thermogravimetric analysis
(TGA) was performed on the polyimide films at a heating
rate of 10°C/min under flowing air and nitrogen. Polymer
densities were obtained at 23°C using thin films (cured at
100, 200 and 300°C for 1 hour in air) and a density gradient
column consisting of aqueous zinc chloride. These results
are given in Table 6.

Example 16

Neat resin moldings were prepared from the copolyimide
powder using the following procedure. The copolyimide
powder (2% offset) was placed in a stainless steel mold
which had been pretreated with a release agent. Various
molding conditions (summarized in Table 4) were used to
form consolidated moldings. The glass transition tempera-
ture (Tg) was determined from the molding flash using
Differential Scanning Calorimetry (DSC) at a heating rate of
20°C per minute. The results are given in Table 4. Neat resin
properties of the molded specimens were also tested.
These properties are summarized in Table 5.

Example 17

Physical and thermal properties were determined for
copolyimide (PI) solutions and thin films which were pre-
pared having a 3% offset ratio and endcapped with phthalic
anhydride. The inherent viscosities (ηinh) were obtained in
copolyimide/NMP solutions (0.5 g/dL) at 25°C, as well as
for the polyamic acids (PAA). Differential scanning calo-
rimetry (DSC) was performed on copolyimide films (dried at
100, 200 and 300°C for 1 hour in air) at a heating rate of
20°C C/min with the glass transition temperature (Tg) taken
at the inflection point in the heat flow vs. temperature curve
and the melting temperature (Tm) taken at the minimum of
the endothermic depression. Thermogravimetric analysis
(TGA) was performed on the polyimide films at a heating
rate of 2.5°C/min under flowing air and nitrogen. Polymer
densities were obtained at 23°C using thin films (cured at
100, 200 and 300°C for 1 hour in air) and a density gradient
column consisting of aqueous zinc chloride. These results
are given in Table 6.
A 10 gauge copper wire was dipped into the various ports or molded directly to form different objects for without the substrates. Various unique applications. 30 powders used to prepare the composites. In this example, the graphite and graphite/copper composites at 230° C. Three point bend geometry testing was performed on the 25 folded in half with the copolyimide to the inside and placed in a stainless steel mold. A piece of aluminum foil could not be removed without destroying the substrates.

Matrix composites were prepared using a 50/50 blend of BPDN/ODPA at a 2% offset and endcapping with phthalic anhydride. Iron, diamond dust, Upilex R® plastic powder, quartz, graphite and graphite/copper combinations were the substrates used to prepare the composites. In this example, the copolyimide serves as a binder for the particles. Table 9 summarizes the fabrication conditions for these composites.

Three point bend geometry testing was performed on the 25 folded in half with the copolyimide to the inside and placed in a stainless steel mold. A piece of aluminum foil could not be removed without destroying the substrates.

The following example is for the preparation of a composite from the copolyimide. A 30% by weight solids in NMP solution of BPDN/ODPA 50/50 copolyimide having a 3% offset ratio was used to solution coat continuous IM-7 carbon fibers (commercially available from Hercules) creating a 3 inch wide unidirectional tape. This tape was then cut into 3x3 inch and 3x6 inch sections (plies) and stacked to form panels which were 12 and 24 plies thick. The panels were consolidated at 300° C. and 5000 psi for 30 minutes to form a consolidated graphite part having a foil backing. The aluminum foil could not be removed without being destroyed.

The following procedure was used to form thermally and mechanically reversible gels from the copolyimides. Several liquid solutions consisting of 10%, 30% and 60% by weight solids in NMP were prepared from 50/50 BPDN/ODPA copolyimides having a 2% offset. The liquid solutions were made through direct synthesis of the copolyimide and by dissolving the required amount of the copolyimide in the solvent. The liquid solutions were allowed to stand for 24 hours before being used in the preparation of the thermally and mechanically reversible gels.
hours at room temperature whereby a thick gel formed. The gelled solutions were then heated until the liquid solution reformed. In addition to heating the gelled solutions, the 10% and 30% by weight gelled solutions were mechanically agitated to reform the liquid solution. The reformed liquid solutions were allowed to stand at room temperature which caused the gel to reform. As a result, the sol-gel process was shown to be both thermally and mechanically reversible. This is demonstrated by the DSC data shown in Table 11.

### Table 11

<table>
<thead>
<tr>
<th>Solids of Gel</th>
<th>1st Run Tm (°C)</th>
<th>2nd Run Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>119</td>
<td>None Detected</td>
</tr>
<tr>
<td>60</td>
<td>178</td>
<td>None Detected</td>
</tr>
</tbody>
</table>

Example 27

Solvent resistance testing was performed on a copolyimide prepared from BPDA/ODPA (50/50) 2% offset polyimide film which had been dried at 300° C. The thin films were weighed and twisted around a steel paper clip which was subsequently placed into a jar containing a specific solvent for 10 days. After removing the films from the jar, they were blotted dry, visually examined, weighed and creased. The results from this test along with the respective solvents which were used are recorded in Table 12.

### Table 12

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Test Temp (°C)</th>
<th>Weight Loss (%)</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
<tr>
<td>Jet Fuel</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
<tr>
<td>Toluene</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
<tr>
<td>MEK</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
<tr>
<td>Methylene Chloride</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
<tr>
<td>Hydraulic Fluid (TSP Based)</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
<tr>
<td>NMP</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
<tr>
<td>THF</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>23</td>
<td>&lt;0.1%</td>
<td>NCC, Creasible</td>
</tr>
</tbody>
</table>

NCC = No Color Change

Example 28

The following procedure was followed to prepare a sprayable dielectric coating. A formulated solution of BPDA/ODPA 50/50 2% offset copolyimide (10% solids in NMP) was applied to different substrates using an airbrush. Examples of these substrates include: glass, ceramic, aluminum, Kapton®, copper, Yttrium stabilized zirconia (YSZ), and Lead Zirconate Titanate (PZT). The coating was initially dried in air at 44° C. and dried at a final temperature of 300° C. for 30 minutes. The film was then metallized and patterned using a standard photolithography process. After the circuit was formed, multiple coats of the copolyimide solution (1 part of BPDA/ODPA 50/50 2% offset to 8 parts of NMP solvent by weight) were sprayed to isolate the newly formed circuit. The sprayed coating was dried in a similar manner and metallized with 300 Angstroms of chrome and 2,000 Angstroms of gold. A circuit was patterned onto the newly coated film using the same photolithography process. This process was repeated multiple times in order to form a multilayer thin film flexible circuit.

Example 30

The following process was used to bond films and foils together. BPDA/ODPA 50/50 2% offset copolyimide (10% solids in NMP) solution was sprayed onto various polyimide films and aluminum/copper foils in order to bond them together. After the film or foil was sprayed with the copolyimide, it was dried at 100 and 250° C. for one hour each in air. The film and foil were stacked and hot pressed at a temperature of 300° C. using 100 psi for 15 minutes to secure the bond. The bonded film could be flexed without delamination showing that it could be used in the formation of ultra-thin multilayer polyimide metal-film laminates.

I claim:

1. A copolyimide having the repeat unit:

   ![Repeat Unit](image)

2. A copolyimide according to claim 1 wherein the copolyimide is terminated with maleic anhydride.

3. A copolyimide according to claim 1 wherein the copolyimide is terminated with phenylethynyl anhydride.

4. A copolyimide according to claim 1 wherein the copolyimide is terminated with ethynyl anhydride.

5. A copolyimide according to claim 1 wherein the copolyimide is terminated with nadic anhydride.

6. A copolyimide according to claim 1 wherein the copolyimide is terminated with vinyl anhydride.

7. A copolyimide according to claim 1 wherein the copolyimide is terminated with benzocyclobutane anhydride.

8. A copolyimide according to claim 1 wherein the copolyimide is terminated with phenylethynyl amine.

9. A copolyimide according to claim 1 wherein the copolyimide is terminated with ethynyl aniline.
10. A copolyimide according to claim 1 wherein the copolyimide is terminated with vinylaniline.

11. A copolyimide according to claim 1 wherein the copolyimide is terminated with allylaniline.

12. A copolyimide according to claim 1 prepared by reacting 4,4'-oxydiphthalic anhydride with 3,4,3',4'-biphenyltetra carboxylic dianhydride and 3,4'-oxydiisocyanate.

13. An article prepared from the copolyimide according to claim 1, wherein the article is selected from the group consisting of: a foam, a tack-free recoatable film, a particle filled thin film and a particle filled thin coating.

14. A particle filled thin film prepared from the copolyimide according to claim 1, wherein the particle is selected from a group consisting of: metal, plastic, ceramic, carbon and boron.

15. A particle filled thin coating prepared from the copolyimide according to claim 1, wherein the particle is selected from a group consisting of: metal, plastic, ceramic, carbon and boron.

16. A copolyimide according to claim 1 prepared by reacting a corresponding tetra acid of 4,4'-oxydiphthalic anhydride with a corresponding tetra acid of 3,4,3',4'-biphenyltetra carboxylic dianhydride and 3,4'-oxydiisocyanate.

17. A copolyimide according to claim 1 prepared by reacting a corresponding di (acid-ester) of 4,4'-oxydiphthalic anhydride with a corresponding di (acid-ester) of 3,4,3',4'-biphenyltetra carboxylic dianhydride and 3,4'-oxydiisocyanate.

* * * * *