POLYIMIDE FOAMS

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See application file for complete search history.

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Primary Examiner—Irina S Zemel

Abstract

A fully imidized, solvent-free polyimide foam having excellent mechanical, acoustic, thermal, and flame resistant properties is produced. A first solution is provided, which includes one or more aromatic dianhydrides or derivatives of aromatic dianhydrides, and may include one or more aromatic diamines, dissolved in one or more polar solvents, along with an effective amount of one or more blowing agents. This first solution may also advantageously include effective amounts respectively of one or more catalysts, one or more surfactants, and one or more fire retardants. A second solution is also provided which includes one or more isocyanates. The first and second solutions are rapidly and thoroughly mixed to produce an admixture, which is allowed to foam—in an open container, or in a closed mold—under ambient conditions to completion produce a foamed product. This foamed product is then cured by high frequency electromagnetic radiation, thermal energy, or a combination thereof. Alternatively, the process is adapted for spraying or extrusion.

31 Claims, No Drawings
POLYIMIDE FOAMS

CLAIM OF BENEFIT OF APPLICATION

This application is a divisional application of commonly-owned patent application Ser. No. 10/779,552, filed Feb. 11, 2004 now U.S. Pat. No. 6,956,066, which, pursuant to 35 U.S.C. § 119, claimed the benefit of priority from provisional patent application Ser. No. 60/446,355, filed on Feb. 11, 2003.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The invention described herein was made in part by employees of the United States Government and may be manufactured and used by and for the Government of the United States for governmental purposes without the payment of any royalties thereon or therefore.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This present invention relates generally to polyimides. It relates in particular to polyimide foams and a process for the preparation of polyimide foams for widespread applications in the aerospace, marine, automotive and building construction industries.

2. Description of the Related Art

Polyimide foams have a number of beneficial attributes for many applications. As a result, they are employed in joining metals to metals or metals to composite structures; as structural foam, having increased structural stiffness without large weight increases; and as low density insulation for thermal and acoustic applications.

Methods for making polyimide foams as disclosed in U.S. Pat. Nos. 5,298,531; 5,122,546; 5,077,318; and 4,900,761 utilize solutions of diamines and dianhydrides or dianhydride derivatives in a low molecular weight alkyl alcohol solvent. Polyimide precursor solutions and powders therefrom are then processed into foams through the expulsion of water and alcohol during a thermal imidization process. Unfortunately, foams prepared by these methods are not available in a wide range of densities, especially very low densities, along with the desired combination of mechanical properties and flame resistance. Moreover, thermal energy must be applied to the precursors to produce the foam, thereby limiting the applicability of the processes.

Polyimide foaming processes as disclosed in U.S. Pat. Nos. 4,738,990; 6,057,379; and 6,133,330 all employ powder precursors. As a result, these processes do not present the widest possible range of applicability, however efficacious they might be.

Polyimide foaming processes as disclosed in U.S. Pat. Nos. 6,057,379 and 4,946,873, as well as U.S. Patent Application Publication 2003/0065044A1, all require the application of microwave radiation to initiate the foaming process. Such a requirement presents a significant limitation on the applicability of these processes.

BRIEF SUMMARY OF THE INVENTION

It is accordingly a primary object of the present invention to overcome difficulties and avoid inadequacies presented by related art processes for the production of polyimide foams. This object is achieved by employing the process of the present invention, which includes preparing a first solution of one or more aromatic dianhydrides or derivatives of aromatic dianhydrides in one or more polar solvents. This first solution additionally includes one or more blowing agents, and advantageously also one or more catalysts, one or more surfactants, and one or more fire retardants, and may also include one or more aromatic diamines. A second solution is provided, which includes one or more isocyanates. The first and second solutions are then mixed rapidly and vigorously to produce an admixture, which is allowed to foam to completion under ambient conditions, without the application of external energy, to produce a foamed product. In one embodiment, the admixture is allowed to foam either in an open container or in a closed mold, and the low density, low-to-medium molecular weight foamed product thereby produced is subsequently polymerized to a high molecular weight product by exposure to high frequency electromagnetic radiation, such as microwave radiation, either alone or followed by thermal energy to finalize cure. Thermal energy may also be used exclusively to cure. In an alternative embodiment, the first and second solutions are mixed in air within a mixing chamber of a spraying system, into which mixing chamber the first and second solutions are individually fed. The resulting admixture is then injected and then immediately sprayed by the spraying system onto the surface of an article, upon which it is allowed to foam to completion at ambient conditions, and is then cured. The first and second solutions can also be combined in a high speed mixer for subsequent extrusion.

The polyimide foams prepared by the process of the present invention have densities ranging from about 0.2 pounds per cubic foot to about 20 pounds per cubic foot. These foams have excellent mechanical, acoustic, thermal, and flame resistant properties including excellent compression rebound, and are therefore highly suitable as insulation materials.

Because the foam precursors are liquid in the present process, and because an input of energy is not required to form the foam, the process of the present invention is appropriate for a wider range of applications than related art processes. Moreover, high yields of foam are provided, with no significant amount of waste to be disposed of afterwards. Finally, the process of the present invention affords a much greater control over density, as well as open/closed cell content of the foam, as compared with prior art processes.

DETAILED DESCRIPTION OF THE INVENTION

According to the process of the present invention, a first solution is provided which is one or more aromatic dianhydrides or derivatives of aromatic dianhydrides, and may include one or more aromatic diamines, dissolved in one or more polar solvents, along with an effective amount of one or more blowing agents. The one or more aromatic dianhydrides are advantageously, but not limited to, pyromellitic dianhydride (PMDA), or 3,3',4,4'-biphenylene tetracarboxylic dianhydride (BTDA), or 4,4'-oxydiphenyl anhydride (ODPA), 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA), and the polar solvents are desirably, but not limited to, N,N-dimethylformamide (DMF), or N,N-dimethylacetamide (DMAc), or N-methylpyrrolidone (NMP). Effective blowing agents are water, methanol, ethanol, acetone, 2-butoxyethanol, ethyl glycol butyl ether (EB), ethylene glycol (E-600), halogen substituted organic compounds such as HFC-141B and HFC-245FA, which are available from Honeywell, triethylamine, and others such as tetrahydrofuran (THF). The aromatic diamines are advantageously, but not limited to, 4,4'-oxydianiline (4,4' ODA), 3,4'-oxydianiline (3,4' ODA), m-phenylenediamine (m-PDA), p-phenylenediamine (p-PDA), 1,3 bis(3-aminoophenoxy)benzene (3-APB), 4,4'...
diaminobenzophenone (4,4’ DABP) and 4,4’ diaminodiphenylsulphone (4,4’ DDS). However, other similar materials may be employed as substitutes.

Highly beneficial results are achieved if the first solution also includes one or more catalysts such as an amine based catalyst or a metallic based catalyst. Suitable amine based catalysts are POLYCAT® 33, POLYCAT® 5, POLYCAT® BL 22, POLYCAT® LV 33, POLYCAT® 18 and DABCO® 8154 amine based catalysts, which are available from Air Products and Chemicals, Inc., as well as NIAX® A-33 amine based catalyst, which is available from OSI Specialities, Inc. A suitable metallic based catalyst is DABCO® K-15 metallic based catalyst, which is available from Air Products and Chemicals, Inc.

Excellent results are obtained if the first solution also includes an effective amount of one or more surfactants. Surfactants which have been employed with success are DC 193, DC 195, DC 197, DC 198, DC 5000 and DC 5598 surfactants, which are available from Dow Coming, as well as NIAX® L-620 and NIAX® L-6900 surfactants, which are available from OSI Specialities, Inc.

It is also especially advantageous if the first solution also includes an effective amount of one or more fire retardants. Suitable fire retardants are ANTI-BLAZE N, ANTI-BLAZE 80, and VIRCOL® 82 fire retardants, which are all available from Rhodia.

According to the process of the present invention, a second solution is provided which includes one or more isocyanates. The one or more isocyanates may be monomeric organic isocyanates, polymeric organic isocyanates, or inorganic isocyanates. Isocyanates which have been beneficially employed are RUBINATE® M (polymeric, NCO content=31.3%, functionality=2.7); RUBINATE® TDI (NCO content=48.3%, functionality=2.0); toluene disocyanate (TDI); methylene disocyanate (MDI); PAPI® 94; and PAPI® 27, all of which are available from Huntsman Polyurethanes.

According to the process of the present invention, the first and second solutions are combined at ambient temperature to produce an admixture, which is then allowed to foam to completion under ambient conditions to produce a foamed product, without the application of external energy in any form.

In one embodiment of the present process, the first and second solutions are thoroughly combined by stirring with a high speed mixer to produce the admixture, and the admixture is allowed to foam to completion in an open container, or alternatively in a closed mold. Once the foaming has been completed, the low density, low-to-medium molecular weight foamed product from the open container or the closed mold is then cured and polymerized to a high molecular weight product by exposure to high frequency electromagnetic radiation, advantageously microwave radiation, either alone or followed by thermal energy to finalize cure. Thermal energy may also be used exclusively to cure. Hereby the foamed product is cured from the inside thereof outwardly, allowing the evolution of volatiles from interior areas of the foamed product, instead of entrapment of the volatiles therein by an outer rind. If desired, the cured foamed product can be post cured by exposure thereof to thermal energy, whereby the cured foamed product is post cured from the outside thereof inwardly.

In another embodiment of the present process, the first and second solutions are thoroughly combined within a mixing chamber of a spraying system, into which mixing chamber the first and second solutions are individually fed. The resulting admixture is sprayed by the spraying system onto the surface of an article, upon which it is allowed to foam to completion. The first and second solutions can also be combined in a high speed mixer for subsequent extrusion.

EXAMPLES

The following examples are illustrative of the present invention, and are not intended to limit the ambit thereof. Densities specified are in accordance with ASTM D-3574-A.

Example 1

One hundred sixty-eight (168) grams of pyromellitic dianhydride (PMDA) were dissolved in two hundred forty (240) grams of N,N-dimethyl formamide (DMF) at approximately 210° F. The solution was held at temperature and stirred until the PMDA was fully dissolved and the solution became clear. The solution was then cooled to approximately 175° F. Once cooled, twenty (20) grams of methanol were added to the solution and stirred. The addition of the methanol produced an exothermic reaction, which increased the temperature of the solution by approximately 25° F. This solution was again cooled, this time to approximately 120° F. A second solution consisting of twenty (20) grams of water, thirty-four (34) grams of surfactant (DC 193), 0.06 grams of DABCO® K-15 catalyst, 0.03 grams of POLYCAT® BL 22 catalyst, 12.5 grams of ethylene glycol (E-600), and 8.6 grams of ANTI-BLAZE N phosphorus based fire retardant, was prepared concurrently. This second solution was stirred at room temperature. This second, room temperature solution was poured into the 120° F. DMF solution and the mixture was stirred for several minutes. The combined solution was again cooled, this time to approximately 100° F. Once cool, 27.4 grams of RUBINATE® M isocyanate was added to 48.4 grams of the DMF solution. The remainder of the DMF solution was cooled to room temperature and stored for later use and given the designation 090403. The combined DMF solution and RUBINATE® M mixture was vigorously stirred with a high speed mixer (about 2000 rpm) for approximately 5-20 seconds. The contents, which began to rise/foam at this point, was immediately transferred to a Pyrex dish where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a conventional 1200-watt microwave oven and cured on high for nine minutes. The resultant foam was bright yellow in color and very tough with a density of 0.35pcf. DSC measurements of the resultant foam indicated full imidization of the material.

Example 2

Two hundred forty-eight (248) grams of 3,3’,4,4’bezophe-none tetracarboxylic dianhydride (BTDA) were dissolved in two hundred forty (240) grams of N,N-dimethylformamide (DMF) at approximately 250° F. The solution was brought to a boil and stirred for approximately fifteen minutes. The partially dissolved solution was then cooled to approximately 180° F. Once cooled, twenty (20) grams of methanol were added to the solution and stirred. The addition of the methanol produced an exothermic reaction that increased the temperature of the solution by approximately 25° F. The addition of the methanol produced a fully dissolved, clear solution. This solution was again cooled, this time to approximately 120° F. A second solution consisting of twenty (20) grams of water, thirty-four (34) grams of surfactant (DC 193), 0.2 grams of DABCO® K-15 catalyst, 0.02 grams of POLYCAT® BL 22 catalyst, 12.5 grams of ethylene glycol (E-600), and 8.6 grams of ANTI-BLAZE N phosphorous-based fire retardant,
was prepared concurrently. This second solution was stirred at room temperature. The second, room temperature solution was poured into the 120° F. DMF solution and stirred for several minutes. The combined solution was again cooled, this time to approximately 100° F. Once cool, 26.9 grams of RUBINATE® M isocyanate was added to 56.1 grams of the DMF solution. The remainder of the DMF solution was cooled to room temperature and stored for later use and given the designation B030303. The combined DMF solution and RUBINATE® M mixture was vigorously stirred with a high speed mixer (about 2000 rpm) for approximately 5-20 seconds. The contents, which began to rise/foam at this point, was immediately transferred to a Pyrex dish where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 5 minutes), it was immediately transferred to a Pyrex dish where it was allowed to rise to ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was removed from the Pyrex dish and placed directly in a conventional 1200-watt microwave oven and cured on high for nine minutes. The resultant foam was dark yellow in color and somewhat brittle with a density of 0.94 pcf. DSC measurements of the resultant foam indicated full imidization of the material.

Example 3

Two hundred twenty-six (226) grams of 3,3',4,4'-biphenyltetrahydroxylic dianhydride (BPDA) were dissolved in two hundred forty (240) grams of N,N-dimethylformamide (DMF) at approximately 250° F. The solution was brought to a boil and stirred for approximately fifteen minutes. The partially dissolved solution was then cooled to approximately 180° F. Once cooled, twenty (20) grams of methanol were added to the solution and stirred. The addition of the methanol produced a slight exothermic reaction that increased the temperature of the solution by approximately 10° F. However, in this case the addition of the methanol did not produce a fully dissolved, clear solution. The DMF/methanol mixture was again heated to 195° F. and stirred for an additional fifteen minutes. The BPDA did not completely dissolve and the resultant mixture was cloudy. The solution was then cooled to approximately 120° F. A second solution consisting of twenty (20) grams of water, thirty-four (34) grams of surfactant (DC 193), 0.04 grams of DABCO K-15, 0.04 grams of POLYCAT® BL 22 catalyst, 12.5 grams of ethylene glycol (E-600), and 8.6 grams of ANTIBLAZE N phosphorous-based fire retardant, was prepared concurrently. This second solution was stirred at room temperature. The second, room temperature solution was poured into the 120° F. DMF mixture and stirred for several minutes. The combined solution was again cooled, this time to approximately 100° F. The combined mixture was cloudy white in color. Once cool, thirty (30) grams of RUBINATE® M isocyanate was added to forty-five (45) grams of the DMF solution. The remainder of the DMF solution was cooled to room temperature and stored for later use and given the designation B030303. The combined DMF and RUBINATE® M mixture was vigorously stirred with a high speed mixer (about 2000 rpm) for approximately 5-20 seconds. The contents, which began to rise/foam at this point, was immediately transferred to a Pyrex dish where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 5 minutes), it was removed from the Pyrex dish and placed directly in a conventional 1200-watt microwave oven and cured on high for nine minutes. The resultant foam was dark yellow in color and very tough with a density of 0.35 pcf. DSC measurements of the resultant foam indicated full imidization of the material.

Example 4

An equal molar solution of pyromellitic dianhydride (PMDA) and 3,3',4,4'-bezophenone tetracarboxylic dianhydride (BTDA) was prepared by mixing 24.7 grams of solution 030403 from Example 1 and 28 grams of solution B030303 from Example 2. The mixture was stirred at room temperature for approximately five minutes. At room temperature, 27.4 grams of RUBINATE® M isocyanate was added to the 52.7 grams dianhydride/DMF solution. This mixture was vigorously stirred with a high speed mixer (about 2000 rpm) for approximately 5-20 seconds. The contents, which began to rise/foam at this point, was immediately transferred to a Pyrex dish where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was removed from the Pyrex dish and placed directly in a conventional 1200-watt microwave oven and cured on high for nine minutes. The resultant foam was dark yellow in color and very tough with a density of 0.59 pcf. DSC measurement of the resultant foam indicated full imidization of the material.

Example 5

Eighty-four (84) grams of pyromellitic dianhydride (PMDA) were dissolved in one hundred twenty (120) grams of N,N-dimethylformamide (DMF) at approximately 210° F. The solution was held at temperature and stirred until the PMDA was fully dissolved and the solution became clear. The solution was then cooled to approximately 175° F. Once cooled, five (5) grams of methanol and five (5) grams of acetone were added and the solution was stirred. The addition of the methanol/acetone produced an exothermic reaction, which increased the temperature of the solution by approximately 15° F. This solution was cooled to approximately 120° F. A second solution consisting of ten (10) grams of water, seventeen (17) grams of surfactant (DC 193), 0.01 grams of DABCO K-15 catalyst, 0.01 grams of POLYCAT® BL 22 catalyst, 6.3 grams of glycol (E-600), and 4.3 grams of ANTIBLAZE N phosphorous based fire retardant, was prepared concurrently. This second solution was stirred at room temperature. The second, room temperature solution was poured into the 120° F. DMF mixture and stirred for several minutes. The combined solution was again cooled, this time to approximately 100° F. Once cool, 27.4 grams of RUBINATE® M isocyanate was added to 48.4 grams of the DMF solution. The remainder of the DMF solution was cooled to room temperature and stored for later use and given the designation B032603a. The combined DMF solution and RUBINATE® M mixture was vigorously stirred with a high speed mixer (about 2000 rpm) for approximately 5-20 seconds. The contents, which began to rise/foam at this point, was immediately transferred to a Pyrex dish where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a conventional 1200-watt microwave oven and cured on high for nine minutes. The resultant foam was bright yellow in color and very tough with a density of 0.94 pcf. DSC measurement of the resultant foam indicated full imidization of the material.
color and extremely tough with a density of 0.35 pcf. DSC measurements of the resultant foam indicated full imidization of the material.

Example 6

Thirty (30) grams of solution 030403 from Example 1 and twenty-one (21) grams of RUBINATE® M isocyanate were mixed together in a container at room temperature and vigorously stirred with a high speed mixer (about 2000 rpm) for approximately 5-20 seconds. The contents, which began to rise/foam at this point, was immediately transferred to a 473 ml closed ceramic mold where it was allowed to rise at ambient conditions. The foam was held in a closed mold at ambient conditions for approximately two and one half hours. (Approximately ten (10) grams of material squeezed out of the mold during the foaming process and six (6) grams were left in the mixing container.) At this point, the foamed product was removed from the mold and placed in a commercial 3000-watt microwave oven and cured at fifty (50) percent power for three minutes, followed by an additional three minutes at seventy (70) percent power, and then another three minutes at full power. The resultant foam of very good quality, dark yellow in color and tough with a density of 1.5 pcf. DSC measurements of the resultant foam indicated full imidization of the material.

Example 7

Flashing from the molding process from Example 6 that had been exposed to ambient conditions for approximately three hours was further compressed and then placed in a commercial 3000-watt microwave oven and cured at fifty (50) percent power for three minutes, followed by an additional three minutes at seventy (70) percent power, and then another three minutes at full power. The resultant foam was very hard, dark yellow in color and extremely tough with a density of approximately 8.5 pcf. DSC measurements of the resultant foam indicated full imidization of the material.

Example 8

A first solution comprising PMDA, DMF, methanol, water, surfactant DC 193, DABCO K-15 catalyst and POLYCAT® BL 22 catalyst, ethylene glycol (E-600), and ANTIBLAZE N phosphorous-based fire retardant, as generally set forth in Example 1 was prepared and placed in a first storage tank. A second solution comprising methylene diisocyanate (MDI) was placed in a second storage tank. Two separate heatable hoses (capable of heating material flowing therethrough at a temperature of 200-250° F.) were individually attached to the first and second storage tanks on first ends thereof, from which the first and second solutions were drawn by a pressure differential and transferred therethrough to a mixing chamber of a spraying system connected to the other ends of the heatable hoses. The first and second solutions were mixed in the air contained within the mixing chamber of the spraying system and applied at a pressure of 1200 psi-1800 psi onto an article, whereupon they began to foam. The resulting exothermic reaction increased the temperature to a value high enough to cure the resulting foamed material. Hereby an article such as a marine vessel fuel tank is effectively protected. Moreover, any other intrinsic shape can be fully covered by foam and protected according to this embodiment of the present invention.

Example 9

Two hundred forty (240) grams of N,N-dimethyl formamide (DMF) was placed in a container. To the DMF was added twenty (20) grams of methanol, twenty (20) grams of water, thirty-four (34) grams of surfactant (DC 193), 0.06 grams of DABCO K-15 catalyst, 0.03 grams of POLYCAT BL 22 catalyst, 12.5 grams of ethylene glycol (E-600), and 8.6 grams of ANTIBLAZE N phosphorous-based fire retardant. Once the solution had been mixed thoroughly, one hundred sixty eight (168) grams of pyromellitic dianhydride (PMDA) was added and an exothermic reaction occurred, raising the temperature of the solution by approximately 50° F. The solution was allowed to cool to approximately 100° F. Once cool, 27.4 grams of RUBINATE® M isocyanate was added to 48.4 grams of the DMF solution. The remainder of the DMF solution was cooled to room temperature and stored for later use and given the designation 1-pot method. The combined DMF solution and RUBINATE® M mixture was vigorously stirred with a high-speed mixer (about 2000 rpm) for approximately 5-20 seconds. The contents, which begin to rise/foam at this point, were immediately transferred to a Pyrex dish where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a conventional 1200-watt microwave oven and cured on high for nine minutes. The resultant foam was bright yellow in color and very tough with a density of 0.39 pcf. DSC measurements of the resultant foam indicated full imidization of the material.

Example 10

A solution consisting of twelve (12) grams of methanol, 6.7 grams of ethyl glycol butyl ether (EB), 18 grams of surfactant (DC 193), 4.1 grams of ANTIBLAZE N phosphorous based fire retardant, 9.2 grams of ethylene glycol (E-600), 10.5 grams of water, 120 grams of N,N-dimethyl formamide (DMF), and 0.05 grams of AS-102 catalyst was prepared and stirred at room temperature. Then, 120 grams of pyromellitic dianhydride (PMDA) was slowly added to this combined solution. The addition of the PMDA into the solution was controlled such that the resultant exothermic reaction did not cause the solution temperature to exceed 190° F. A temperature of about 190° F. was maintained during the stirring of the solution and the addition of PMDA. Once combined, the resultant solution was cooled to approximately 98° F. This solution was given the designation of Part B. Once cool, 132.6 grams of RUBINATE® M isocyanate, given the designation Part A, was added to the solution. The Part B/Part A mixture was vigorously stirred with a high-speed mixer for approximately 5-20 seconds. The contents, which begin to rise/foam at this point, was immediately transferred to an open mold where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a commercial microwave oven and cured at high for nine minutes. The resultant foam was bright yellow in color and very tough with a density of 0.39 pcf. DSC measurements of the resultant foam indicated full imidization of the material.

Tables 1 and 2 display variations to Example 10 and the resultant change to the final foam density, with Table 1 displaying the variations in weight corresponding to the % variations in Table 2. The components that were varied are underlined. Thermal conductivity was measured by ASTM C-518 to be 0.534 Btu/hr-ft²° F at room temperature.
TABLE 1

<table>
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<tr>
<th>Example</th>
<th>PMDA (g)</th>
<th>DC193 (g)</th>
<th>ANTIBLAZE (g)</th>
<th>E600 (g)</th>
<th>H2O (g)</th>
<th>AS-102 (g)</th>
<th>Temperature (°F)</th>
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*MDI = RUBINATE ® M*

TABLE 2

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<tr>
<th>Example</th>
<th>PMDA (wt %)</th>
<th>DC193 (wt %)</th>
<th>ANTIBLAZE (wt %)</th>
<th>E600 (wt %)</th>
<th>H2O (wt %)</th>
<th>AS-102 (wt %)</th>
<th>Part B/Part A</th>
<th>Temperature (°F)</th>
<th>Ratio</th>
<th>Resultant Foam Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>39.9</td>
<td>39.9</td>
<td>3.99</td>
<td>2.23</td>
<td>5.98</td>
<td>1.36</td>
<td>3.06</td>
<td>3.49</td>
<td>0.17</td>
<td>Excellent Foam with a Density of 0.34 pcf</td>
</tr>
<tr>
<td>10-A</td>
<td>39.9</td>
<td>39.9</td>
<td>3.99</td>
<td>2.23</td>
<td>5.98</td>
<td>1.36</td>
<td>3.06</td>
<td>3.49</td>
<td>0.17</td>
<td>Density Decreased to 0.3 pcf</td>
</tr>
<tr>
<td>10-B</td>
<td>39.9</td>
<td>39.9</td>
<td>3.99</td>
<td>2.23</td>
<td>5.98</td>
<td>1.36</td>
<td>3.06</td>
<td>3.49</td>
<td>0.17</td>
<td>Density Decreased to 0.28 pcf and foam was Rigid</td>
</tr>
<tr>
<td>10-C</td>
<td>39.9</td>
<td>39.9</td>
<td>3.99</td>
<td>2.23</td>
<td>5.98</td>
<td>1.36</td>
<td>3.06</td>
<td>3.49</td>
<td>0.17</td>
<td>Density Increased to 0.37 pcf and foam was flexible</td>
</tr>
<tr>
<td>10-D</td>
<td>39.7</td>
<td>39.7</td>
<td>3.97</td>
<td>2.22</td>
<td>5.96</td>
<td>1.36</td>
<td>3.06</td>
<td>3.84</td>
<td>0.17</td>
<td>Density Increased to 0.4 pcf and foam was Very Rigid</td>
</tr>
<tr>
<td>10-E</td>
<td>40.0</td>
<td>40.0</td>
<td>4.00</td>
<td>2.23</td>
<td>6.00</td>
<td>1.37</td>
<td>3.07</td>
<td>3.17</td>
<td>0.17</td>
<td>Extremely Fast Reaction and Foam was Rigid</td>
</tr>
<tr>
<td>10-F</td>
<td>39.9</td>
<td>39.9</td>
<td>3.99</td>
<td>2.23</td>
<td>5.98</td>
<td>1.36</td>
<td>3.06</td>
<td>3.49</td>
<td>0.17</td>
<td>Density Increased Slightly to 0.36 pcf</td>
</tr>
<tr>
<td>10-G</td>
<td>39.9</td>
<td>39.9</td>
<td>3.99</td>
<td>2.23</td>
<td>5.98</td>
<td>1.36</td>
<td>3.06</td>
<td>3.49</td>
<td>0.17</td>
<td>Density Increased Slightly to 0.36 pcf</td>
</tr>
</tbody>
</table>

*Part A = RUBINATE ® M*

Example 11

A solution consisting of twelve (12) grams of methanol, 6.7 grams of ethyl glycol butyl ether (EB), 18 grams of surfactant (DC 193), 4.1 grams of ANTIBLAZE N phosphorous based fire retardant, 9.2 grams of ethylene glycol (E-600), 10.5 grams of water, and 0.5 grams of catalyst (AS-102), was prepared and stirred at room temperature. A second solution consisting of 120 grams of N,N-dimethyl formamide (DMF) and 2 grams of 4,4'-oxydianiline (ODA) was also prepared at room temperature. The first methanol solution was then added to the second DMF2 solution and stirred at room temperature. Then, 120 grams of pyromellitic dianhydride (PMDA) was slowly added to this combined solution. The addition of the PMDA into the solution was controlled such that the resultant exothermic reaction did not cause the solution temperature to exceed 190° F. A temperature of about 190° F. was maintained during the stirring of the solution and the addition of PMDA. Once combined, the resultant solution was cooled to approximately 98° F. This solution was given the designation of Part B. Once cool, 133.5 grams of RUBINATE® M isocyanate, given the designation Part A, was added to the solution. The Part B/Part A mixture was vigorously stirred with a high-speed mixer for approximately 5-20 seconds. The contents, which begin to rise/foam at this point, were immediately transferred to an open mold where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a commercial microwave oven and cured. The resultant foam was bright yellow in color and very tough with a density of 0.40 pcf. Thermal conductivity was measure by ASTM C-518 to be 0.269 Btu-in/hr-ft-°F at room temperature.

Example 12

A solution consisting of twelve (12) grams of methanol, 6.7 grams of ethyl glycol butyl ether (EB), 18 grams of surfactant (DC 193), 4.1 grams of ANTIBLAZE N phosphorous based fire retardant, 9.2 grams of ethylene glycol (E-600), 10.5 grams of water, and 0.5 grams of AS-102 catalyst was prepared and stirred at room temperature. A second solution consisting of 120 grams of N,N-dimethyl formamide (DMF2) and 8 grams of 4,4'-oxydianiline (ODA) was also prepared at room temperature. The first methanol solution was then added to the second DMF solution and stirred at room temperature. Then, 120 grams of pyromellitic dianhydride (PMDA) was slowly added to this combined solution. The addition of the PMDA into the solution was controlled such that the resultant exothermic reaction did not cause the solution temperature to exceed 190° F. A temperature of about 190° F. was maintained during the stirring of the solution and the addition of PMDA. Once combined, the resultant solution was cooled to approximately 98° F. This solution was given the designation of Part B. Once cool, 136.1 grams of RUBINATE® M isocyanate, given the designation Part A, was added to the solution. The Part B/Part A mixture was vigorously stirred with a high-speed mixer for approximately 5-20 seconds. The contents, which begin to rise/foam at this point, were immediately transferred to an open mold where it was allowed to rise at ambient conditions. Once the foam was no
longer tacky and was somewhat rigid (about 10 minutes), it was placed in a commercial microwave oven and cured. The resultant foam was bright yellow in color and very tough with a density of 0.51 pcf.

Examples 12A-12P

Other polyimide foams were made by varying the component contents of Example 12. Tables 3 and 4 display variations to Example 12. The weight percentages of each component of Part A and the B/A mix ratios are shown in Table 4. The components that were varied are underlined. Table 4 also provides a brief description of the final foam product. For Examples 12-A through 12-N in Tables 3 and 4, the procedures illustrated in Example 12 were followed. Only the amounts of various components were varied. For Examples 12-O and 12-P, the component contents of Example 12 were used, but the temperature of Part B was varied prior to the addition of Part A. All examples resulted in foams of varying quality and properties.

### TABLE 3

<table>
<thead>
<tr>
<th>Example Number</th>
<th>PMDA</th>
<th>DMF</th>
<th>METH</th>
<th>DC193</th>
<th>ANTIBLAZE</th>
<th>E600</th>
<th>H2O</th>
<th>AS-102</th>
<th>4,4'ODA</th>
<th>Temperature</th>
<th>MDI3</th>
</tr>
</thead>
<tbody>
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<td>12</td>
<td>120</td>
<td>120</td>
<td>12</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>136.1</td>
</tr>
<tr>
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<td>120</td>
<td>12</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>149.7</td>
</tr>
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<td>120</td>
<td>12</td>
<td>6.7</td>
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<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
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<td>163.3</td>
</tr>
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<td>6.7</td>
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<td>4.1</td>
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<td>0.5</td>
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<td>122.5</td>
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<td>6.7</td>
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<td>4.1</td>
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<td>141.4</td>
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<td>120</td>
<td>12</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>130.8</td>
</tr>
<tr>
<td>12-F</td>
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<td>120</td>
<td>13.2</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>122.5</td>
</tr>
<tr>
<td>12-G</td>
<td>120</td>
<td>120</td>
<td>14.4</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>137.2</td>
</tr>
<tr>
<td>12-H</td>
<td>120</td>
<td>120</td>
<td>10.8</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>135.6</td>
</tr>
<tr>
<td>12-I</td>
<td>120</td>
<td>120</td>
<td>12</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>136.5</td>
</tr>
<tr>
<td>12-J</td>
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<td>120</td>
<td>12</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>135.7</td>
</tr>
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<td>120</td>
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<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>135.6</td>
</tr>
<tr>
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<td>120</td>
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<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>137.2</td>
</tr>
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<td>12-M</td>
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<td>120</td>
<td>12</td>
<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>135.6</td>
</tr>
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<td>12-N</td>
<td>120</td>
<td>120</td>
<td>12</td>
<td>6.7</td>
<td>18</td>
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<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>135.7</td>
</tr>
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<td>120</td>
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<td>98° F.</td>
<td>135.6</td>
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<td>6.7</td>
<td>18</td>
<td>4.1</td>
<td>9.2</td>
<td>10.5</td>
<td>0.5</td>
<td>98° F.</td>
<td>135.7</td>
</tr>
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</table>

3MDI = RUBINATE ® M

### TABLE 4

<table>
<thead>
<tr>
<th>Example Number</th>
<th>PMDA</th>
<th>DMF</th>
<th>METH</th>
<th>DC193</th>
<th>ANTIBLAZE</th>
<th>E600</th>
<th>H2O</th>
<th>AS-102</th>
<th>4,4'ODA</th>
<th>Temperature</th>
<th>Part B/A2</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>38.8</td>
<td>38.8</td>
<td>3.88</td>
<td>2.17</td>
<td>5.83</td>
<td>1.33</td>
<td>2.98</td>
<td>3.40</td>
<td>0.16</td>
<td>2.59</td>
<td>98° F.</td>
<td>2.27 Excellent Foam with a Density of 0.51 pcf</td>
</tr>
<tr>
<td>12-A</td>
<td>38.8</td>
<td>38.8</td>
<td>3.88</td>
<td>2.17</td>
<td>5.83</td>
<td>1.33</td>
<td>2.98</td>
<td>3.40</td>
<td>0.16</td>
<td>2.59</td>
<td>98° F.</td>
<td>2.06 Density Decreased to 0.47 pcf</td>
</tr>
<tr>
<td>12-B</td>
<td>38.8</td>
<td>38.8</td>
<td>3.88</td>
<td>2.17</td>
<td>5.83</td>
<td>1.33</td>
<td>2.98</td>
<td>3.40</td>
<td>0.16</td>
<td>2.59</td>
<td>98° F.</td>
<td>1.89 Density Decreased to 0.45 pcf and foam was rigid</td>
</tr>
<tr>
<td>12-C</td>
<td>38.8</td>
<td>38.8</td>
<td>3.88</td>
<td>2.17</td>
<td>5.83</td>
<td>1.33</td>
<td>2.98</td>
<td>3.40</td>
<td>0.16</td>
<td>2.59</td>
<td>98° F.</td>
<td>2.52 Density Increased to 0.54 pcf and foam was flexible</td>
</tr>
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<td>1.28</td>
<td>2.87</td>
<td>3.27</td>
<td>0.16</td>
<td>2.49</td>
<td>98° F.</td>
<td>2.27 Density Increased to 0.69 pcf and foam was less flexible</td>
</tr>
<tr>
<td>12-E</td>
<td>40.4</td>
<td>36.4</td>
<td>4.04</td>
<td>2.26</td>
<td>6.06</td>
<td>1.38</td>
<td>3.10</td>
<td>3.54</td>
<td>0.17</td>
<td>2.69</td>
<td>98° F.</td>
<td>2.27 Very Dense, Liquid Mass, Difficult to mix</td>
</tr>
<tr>
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<td>38.7</td>
<td>38.7</td>
<td>4.26</td>
<td>2.16</td>
<td>5.80</td>
<td>1.32</td>
<td>2.07</td>
<td>3.38</td>
<td>0.16</td>
<td>2.58</td>
<td>98° F.</td>
<td>2.27 Density Decreased to 0.45 pcf</td>
</tr>
<tr>
<td>12-G</td>
<td>38.5</td>
<td>38.5</td>
<td>4.62</td>
<td>2.15</td>
<td>5.78</td>
<td>1.32</td>
<td>2.95</td>
<td>3.37</td>
<td>0.16</td>
<td>2.57</td>
<td>98° F.</td>
<td>2.27 Foamerner, Liquid Mass, Difficult to mix</td>
</tr>
<tr>
<td>12-H</td>
<td>39.0</td>
<td>39.0</td>
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</tr>
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<td>1.32</td>
<td>3.26</td>
<td>3.39</td>
<td>0.16</td>
<td>2.58</td>
<td>98° F.</td>
<td>2.27 Flexible Mass, Slight Increase in Density to 0.54 pcf</td>
</tr>
</tbody>
</table>
Example 13

A solution consisting of twelve (12) grams of methanol, 6.7 grams of ethyl glycol butyl ether (EB), 18 grams of surfactant (DC 193), 4.1 grams of ANTIBLAZE N phosphorus based fire retardant, 9.2 grams of ethylene glycol (E-600), 10.5 grams of water, and 0.5 grams of AS-102 catalyst was prepared and stirred at room temperature. The first methanol solution was then added to the second DMF solution and stirred at room temperature. Then, 120 grams of pyromellitic dianhydride (PMDA) was slowly added to this combined solution. The addition of the PMDA into the solution was controlled such that the resultant exothermic reaction did not cause the solution temperature to exceed 190°F. A temperature of about 190°F was maintained during the stirring of the solution and the addition of PMDA. Once combined, the resultant solution was cooled to approximately 98°F. This solution was given the designation of Part B. Once cool, 154.2 grams of RUBINATE® M isocyanate, given the designation Part A, was added to the solution. The Part B/Part A mixture was vigorously stirred with a high-speed mixer for approximately 5-20 seconds. The contents, which begin to rise/foam at this point, were immediately transferred to an open mold where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a commercial microwave oven and cured. The resultant foam was bright yellow in color and very tough with a density of approximately 0.48 pcf.

Example 14

A solution consisting of twelve (12) grams of methanol, 6.7 grams of ethyl glycol butyl ether (EB), 18 grams of surfactant (DC 193), 4.1 grams of ANTIBLAZE N phosphorus based fire retardant, 9.2 grams of ethylene glycol (E-600), 10.5 grams of water, and 0.5 grams of AS-102 catalyst was prepared and stirred at room temperature. A second solution consisting of 120 grams of N,N-dimethyl formamide (DMF) and 4.3 grams of m-phenylene diamine (m-PDA) was also prepared at room temperature. The first methanol solution was then added to the second DMF solution and stirred at room temperature. Then, 120 grams of pyromellitic dianhydride (PMDA) was slowly added to this combined solution. The addition of the PMDA into the solution was controlled such that the resultant exothermic reaction did not cause the solution temperature to exceed 190°F. A temperature of about 190°F was maintained during the stirring of the solution and the addition of PMDA. Once combined, the resultant solution was cooled to approximately 98°F. This solution was given the designation of Part B. Once cool, 134.5 grams of RUBINATE® M isocyanate, given the designation Part A, was added to the solution. The Part B/Part A mixture was vigorously stirred with a high-speed mixer for approximately 5-20 seconds. The contents, which begin to rise/foam at this point, were immediately transferred to an open mold where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a commercial microwave oven and cured. The resultant foam was bright yellow in color and very tough with a density of approximately 0.48 pcf.
tion temperature to exceed 190° F. A temperature of about 190° F was maintained during the stirring of the solution and the addition of PMDA. Once combined, the resultant solution was cooled to approximately 98° F. This solution was given the designation of Part B. Once cool, 89 grams of RUBI-NATE® TDI isocyanate, given the designation Part A, was added to the solution. The Part B/Part A mixture was vigorously stirred with a high-speed mixer for approximately 5-20 seconds. The contents, which begin to rise/foam at this point, were immediately transferred to an open mold where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a commercial microwave oven and cured. The resultant foam was bright yellow in color and very tough with a density of approximately 0.48 pcf.

Example 16

A solution consisting of twelve (12) grams of methanol, 6.7 grams of ethyl glycol butyl ether (EB), 18 grams of surfactant (DC 193), 4.1 grams of ANTIBLAZE N® phosphorous based fire retardant, 9.2 grams of ethylene glycol (E-600), 10.5 grams of water, and 0.5 grams of AS-102 catalyst was prepared and stirred at room temperature. A second solution consisting of 120 grams of N,N-dimethyl formamide (DMF) and 8 grams of 4,4'-oxydianiline (ODA) was also prepared at room temperature. The first methanol solution was then added to the second DMF solution and stirred at room temperature. Then, 120 grams of pyromellitic dianhydride (PMDA) was slowly added to this combined solution. The addition of the PMDA into the solution was controlled such that the resultant exothermic reaction did not cause the solution temperature to exceed 190° F. A temperature of about 190° F was maintained during the stirring of the solution and the addition of PMDA. Once combined, the resultant solution was cooled to approximately 98° F. This solution was given the designation of Part B. Once cool, 128 grams of RUBI-NATE® 44 (pure methylene diisocyanate, MDI), given the designation Part A, was added to the solution. The Part B/Part A mixture was vigorously stirred with a high-speed mixer for approximately 5-20 seconds. The contents, which begin to rise/foam at this point, were immediately transferred to an open mold where it was allowed to rise at ambient conditions. Once the foam was no longer tacky and was somewhat rigid (about 10 minutes), it was placed in a commercial microwave oven and cured. The resultant foam was bright yellow in color and very tough with a density of approximately 0.48 pcf.

The foamed products prepared according to the embodiments described above display outstanding flame resistance and very low smoke production properties. Moreover, when these foams are placed in contact with a flame, they do not burn, but emit only a minimal amount of smoke. The foams retain their shape and barely shrink after being subjected to high flame temperatures. In addition to the applications detailed above, the polyimide foams prepared according to the present invention can be placed inside the hull of a ship and secured between the bulkheads. Furthermore, foamed material can be cut to size after final curing and firmly adhered to an article such as a marine vessel fuel tank by means of a wrapping system, adhesive or mechanical attachment.

The invention claimed is:

1. A random copolymeric polyimide foam prepared by combining components comprising one or more aromatic dianhydrides, one or more aromatic diamines, and one or more isocyanates, said foam further comprising both random molecular weight imide units and random molecular weight copolymeric units prepared by the reaction of the isocyanates with the random molecular weight imide units.

2. The random copolymeric polyimide foam of claim 1, wherein the weight percentage of aromatic dianhydride is from about 30% to about 80%, the weight percentage of aromatic diamine is from about 0.5% to about 15%, and the weight percentage of isocyanate is from about 10% to about 50%.

3. The random copolymeric polyimide foam of claim 1, wherein the one or more aromatic diamines is one or more members selected from the group consisting of 4,4'-oxydianiline; 3,4'-oxydianiline; m-phenylenediamine; p-phenylenediamine; 1.3 bis(3-aminophenoxy)benzene; 4,4'diaminobenzophenone; and 4,4diaminodiphenylsulphone.

4. The random copolymeric polyimide foam of claim 1, wherein the one or more aromatic dianhydrides is one or more members selected from the group consisting of pyromellitic dianhydride; 3,3',4,4'-bezophenone tetracarboxylic dianhydride; 4,4'-oxydiphthalic anhydride; and 3,3',4,4' biphenyl tetracarboxylic dianhydride.

5. The random copolymeric polyimide foam of claim 1, wherein the one or more isocyanates is one or more members selected from the group consisting of monomeric organic isocyanates, polymeric organic isocyanates, and inorganic isocyanates.

6. The random copolymeric polyimide foam of claim 1, having a density of from about 0.2 pounds/ft³ to about 20 pounds/ft³, whereby the expansion of the polyimide foam is restrained while foaming.

7. The random copolymeric polyimide foam of claim 1, having a density of from about 0.2 pounds/ft³ to about 1 pounds/ft³, whereby the aromatic polyimide foam is allowed to freely expand while foaming.

8. The random copolymeric polyimide foam of claim 1, additionally comprising one or more catalysts.

9. The random copolymeric polyimide foam of claim 8, wherein the one or more catalysts is one or more members selected from the group consisting of amine based catalysts and metallic based catalysts.

10. The random copolymeric polyimide foam of claim 1, additionally comprising one or more surfactants.

11. The random copolymeric polyimide foam of claim 1, additionally comprising one or more fire retardants.

12. The random copolymeric polyimide foam of claim 1, additionally comprising one or more polar solvents.

13. The random copolymeric polyimide foam of claim 12, wherein the one or more polar solvents is one or more members selected from the group consisting of N,N-dimethylformamide; N,N-dimethylacetamide, and N-methylpyrrolidone.

14. The random copolymeric polyimide foam of claim 1, additionally comprising one or more blowing agents.

15. The random copolymeric polyimide foam of claim 14, wherein the one or more blowing agents is one or more members selected from the group consisting of water, methanol, ethanol, acetone, 2-butoxyethanol, ethyl glycol butyl ether, ethylene glycol, halogen substituted organic compound, and ether.

16. The random copolymeric polyimide foam of claim 15, wherein the ether is a member selected from the group consisting of tetrahydrofuran.
with the random molecular weight imide units, and said foam having a density of from about 0.2 pounds/ft$^3$ to 0.8 pounds/ft$^3$.

18. The random copolymeric polyimide foam of claim 17, wherein said aromatic polyimide foam is allowed to freely expand while foaming.

19. The random copolymeric polyimide foam of claim 17, wherein the weight percentage of aromatic dianhydride is from about 30% to about 80%, the weight percentage of aromatic diamine is from about 0.5% to about 15%, and the weight percentage of isocyanate is from about 10% to about 50%.

20. The random copolymeric polyimide foam of claim 17, wherein the one or more aromatic diamines is one or more members selected from the group consisting of 4,4'oxydianline; 3,4oxydianline; m-phenylenediamine; p-phenylenediamine; 1,3 bis(3-aminophenoxy)benzene; 4,4'diaminobenzophenone; and 4,4'diaminodiphenylsulphone.

21. The random copolymeric polyimide foam of claim 17, wherein the one or more aromatic dianhydrides is one or more members selected from the group consisting of pyromellitic dianhydride; 3,3',4,4'-bezophenone tetracarboxylic dianhydride; 4,4'-oxydiphthalic anhydride; and 3,3',4,4'biphenyl tetracarboxylic dianhydride.

22. The random copolymeric polyimide foam of claim 17, wherein the one or more isocyanates is one or more members selected from the group consisting of monomeric organic isocyanates, polymeric organic isocyanates, and inorganic isocyanates.

23. The random copolymeric polyimide foam of claim 17, additionally comprising one or more catalysts.

24. The random copolymeric polyimide foam of claim 23, wherein the one or more catalysts is one or more members selected from the group consisting of amine based catalysts and metallic based catalysts.

25. The random copolymeric polyimide foam of claim 17, additionally comprising one or more surfactants.

26. The random copolymeric polyimide foam of claim 17, additionally comprising one or more fire retardants.

27. The random copolymeric polyimide foam of claim 17, additionally comprising one or more polar solvents.

28. The random copolymeric polyimide foam of claim 27, wherein the one or more polar solvents is one or more members selected from the group consisting of N,N-dimethylformamide; N,N-dimethylacetamide; and N-methylpyrroldione.

29. The random copolymeric polyimide foam of claim 17, additionally comprising one or more blowing agents.

30. The random copolymeric polyimide foam of claim 29, wherein the one or more blowing agents is one or more members selected from the group consisting of water, methanol, ethanol, acetone, 2-butoxyethanol, ethyl glycol butyl ether, ethylene glycol, halogen substituted organic compound, and ether.

31. The random copolymeric polyimide foam of claim 30, wherein the ether is a member selected from the group consisting of tetrahydrofuran.