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(54) Title: ALIPHATIC THERMOPLASTIC POLYURETHANES MADE FROM TELECHELIC N-ALKYLATED POLYAMIDES

(57) Abstract: This invention relates to aliphatic polymers made from aliphatic polyisocyanates and low molecular weight polyamide oligomers and telechelic polyamides (including copolymers) containing N-alkylated amide groups in the backbone structure. The described telechelic polyamides are used as the soft segment in the described TPU. These telechelic polyamides are unique in that they have an unexpectedly low glass-transition (desirably 30 degrees C or lower) which gives the resulting aliphatic polymers have a unique combination of properties making them suitable for certain applications and end uses.

ALIPHATIC THERMOPLASTIC POLYURETHANES MADE FROM TELECHELIC N-ALKYLATED POLYAMIDES

FIELD OF INVENTION

[0001] The invention relates to aliphatic polymers made using telechelic polyamides, including those that are liquid below about 70°C and can be reacted into other polymer networks to impart desirable properties.

BACKGROUND OF THE INVENTION

[0002] Thermoplastic polyurethanes (TPU) are useful materials well known in the art. They are generally prepared by reacting a polyisocyanate with a polyol and optionally a chain extender. The resulting materials have many useful properties and are used in a wide variety of applications.

[0003] TPU contain hard segments and soft segments, where the soft segments are typically polyester based or polyether based. Polyester TPU suffer from hydrolytic degradation while polyether TPU are prone to oxidative and/or thermal degradation. There is an ongoing need for TPU materials that have the expected useful properties but which also provide improved hydrolytic, oxidative and/or thermal stability.

[0004] There is also a desire to improve the adhesion of TPU materials to polar materials such as polyamides or polyesters, for example Nylon-6,6. Currently the ability to use TPU materials in combination with polar materials is limited due to the relatively poor adhesion between existing TPU materials and polar materials, especially where the application involves combining a layer of TPU material with a layer of polar material. The adhesion between the layer is too weak to meet the requirements for many applications where such a layer combination would otherwise be very useful. Thus, TPU cannot be used in many applications requiring high levels of adhesion between layers of TPU and other materials, especially polar materials. There is a continuing need for TPU materials with adhesion to other materials, especially polar materials, that would allow TPU to be used in applications where good/improved adhesion to other materials, especially polar materials, is required.

[0005] Overall there is a continuing need for an improved TPU material that has the expected useful properties of a polyether and/or polyester TPU but also provides improved hydrolytic, oxidative and/or thermal stability, improved adhesion to polar materials such as polyamides or polyesters, and some combination thereof.

SUMMARY OF THE INVENTION

[0006] This invention relates to aliphatic polymers made from low molecular weight polyamide oligomers and telechelic polyamides (including copolymers) that include N alkylated amide groups in the backbone structure. The described telechelic polyamides are used as the soft segment in the described TPU. These telechelic polyamides are unique in their ability to be processed as liquids at temperatures from 20 to 50 or 80°C. While not wishing to be bound by theory, it is believed this may be due to their having unexpectedly low glass-transition temperatures which makes them suitable for further reaction and polymerization, allowing for the formation of the described TPU. The resulting aliphatic polymers have a unique combination of properties making them suitable for certain applications and end uses.

[0007] The invention provides a polymer composition that includes the reaction product of: (i) a polyol component comprising a telechelic polyamide; and (ii) an aliphatic polyisocyanate component; and optionally (iii) a chain extender component; wherein the telechelic polyamide: (a) has repeat units derived from polymerizing monomers connected by linkages between the repeat units and functional end groups selected from carboxyl or primary or secondary amine, wherein at least 70 mole percent of telechelic polyamide have exactly two functional end groups of the same functional type selected from the group consisting of amino or carboxylic end groups; (b) has a polyamide segment comprising at least two amide linkages characterized as being derived from reacting an amine with a carboxyl group, and said polyamide segment comprising repeat units derived from polymerizing two or more of monomers selected from lactams, aminocarboxylic acids, dicarboxylic acids, and diamines; (c) wherein at least 10 percent of the total number of the heteroatom containing linkages connecting hydrocarbon type linkages are characterized as being amide linkages; and (d) wherein at least 25 percent of the amide linkages are characterized as being tertiary amide linkages.

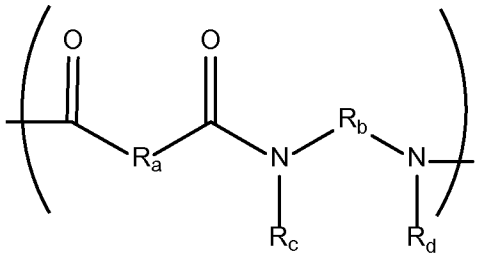
[0008] The invention provides the described polymer compositions wherein said polyamide segment of feature (b) is characterized as meeting at least one of the following conditions: (i) where said amide linkages are derived from polymerizing amide forming monomers and at least 90 mole percent of said monomers are selected from the group consisting of lactams and aminocarboxylic acid monomers such that said polyamide is a copolymer of at least two different monomers; or (ii) where said amide linkages are

derived from polymerizing amide forming monomers and at least 90 mole percent of said monomers are combined amounts of dicarboxylic acid and diamine monomers such that said polyamide is a terpolymer of at least three different monomers; or (iii) where said amide linkages are derived from polymerizing a combination of dicarboxylic acid, diamine and either lactam and/or aminocarboxylic acid monomers such that the total dicarboxylic acid monomer(s) and the diamine monomer(s) are present at 10 mole percent or more and the total lactam and/or aminocarboxylic acid monomers are present in the monomer blend at 10 mole percent or more.

[0009] The invention provides the described polymer compositions wherein at least 50 weight percent of said telechelic polyamide is made up of repeating units derived from monomers selected from the group of lactam monomers, aminocarboxylic acid monomers, dicarboxylic acid monomers, and diamine monomers.

[0010] The invention provides the described polymer compositions wherein at least 10 weight percent of said polymer is made up of repeating units derived from monomers selected from the group of lactam monomers, aminocarboxylic acid monomers, dicarboxylic acid monomers, and diamine monomers.

[0011] The invention provides the described polymer compositions wherein at least 50 weight percent of said polyamide segment comprises repeat units of the structure:



wherein R_a is the alkylene portion of the dicarboxylic acid and is a cyclic, linear, or branched alkylene of 2 to 36 carbon atoms, optionally including up to 1 heteroatom per 3 or 10 carbon atoms of the diacid; and wherein R_b is a direct bond or a linear or branched alkylene group of 2 to 60 carbon atoms and R_c and R_d are individually a linear or branched alkyl group of 1 to 8 carbon atoms, or R_c and R_d connect together to form a single linear or branched alkylene group of 1 to 8 carbon atoms or optionally with one of R_c and R_d is connected to R_b at a carbon atom, more desirably R_c and R_d being an alkyl group of 1 or 2 to 4 carbon atoms.

[0012] The invention provides a polymer composition that includes the reaction product of: (i) a polyol component that includes a telechelic polyamide; and (ii) an aliphatic polyisocyanate component; and optionally (iii) a chain extender component; wherein the telechelic polyamide includes: (a) two functional end groups selected from hydroxyl, carboxyl, or primary or secondary amine; and (b) a polyamide segment wherein: (i) said polyamide segment comprises at least two amide linkages characterized as being derived from reacting an amine with a carboxyl group; (ii) said polyamide segment comprises repeat units derived from polymerizing two or more monomers selected from the group consisting of lactam monomers, aminocarboxylic acids monomers, dicarboxylic acids monomers, and diamine monomers; and (iii) at least 25 mole percent of the amide linkages are derived from reacting a secondary amine group with a carboxyl group; where said telechelic polyamide is characterized as a liquid with a viscosity of less than 100,000 cps at 70°C as measured by a Brookfield circular disc viscometer with the circular disc spinning at 5 rpm; and wherein said telechelic polyamide is characterized by a number average molecular weight from about 200 to 10,000 g/mole and comprises a diversity of amide forming repeating units disrupting hydrogen bonding between amide components.

[0013] The invention provides the described polymer compositions wherein the reaction product further includes one or more polyether segments, polyester segments and/or polycarbonate segments, wherein said segments are chemically bound into said reaction product or physically blended with said reaction product.

[0014] The invention provides the described polymer compositions wherein component (ii), the aliphatic polyisocyanate component, comprises isophorone diisocyanate (IPDI), 1,4-cyclohexyl diisocyanate (CHDI), hexamethylene diisocyanate (HDI), 4,4'-Methylene dicyclohexyl diisocyanate (H_{12} MDI), 1,6-diisocyanato-2,2,4,4-tetramethyl hexane (TMDI), 1,10-decane diisocyanate, trans-dicyclohexylmethane diisocyanate (HMDI), xylylene diisocyanate (XDI), m-tetramethyl xylylene diisocyanate (TMXDI), or any combination thereof.

[0015] The invention provides the described polymer compositions wherein component (iii), the chain extender component, comprises one or more short chain glycols having from about 2 to about 20 carbon atoms.

[0016] The invention provides the described polymer compositions wherein component (iii), the chain extender component, comprises ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, triethylene glycol, cis-trans-isomers of cyclohexyl dimethylol, neopentyl glycol, 1,4-butanediol, 1,6-hexandiol, 1,3-butanediol, and 1,5-pentanediol, benzene glycol (HQEE), xylylene glycols, resorcinol, catechol, 1,3-propanediol, 1,12-dodecandiol, 1,9-nonanediol or any combinations thereof.

[0017] The invention provides an article comprising any of the polymer compositions described herein.

[0018] The invention provides the described article wherein the article is an injection molded article, an article of automotive exterior, an electronic component, or an extruded film.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Telechelic polymers, defined as macromolecules that contain two reactive end groups, can be used as cross-linkers, chain extenders, and important building blocks for various macromolecular structures, including block and graft copolymers, star, hyperbranched or dendritic polymers. Telechelic polymers of the polydiene, polyester, polyether, and polycarbonate type are well known in the art. These prior art telechelic polymers with functional end groups selected from primary or secondary hydroxyl, primary or secondary amine, and carboxylic acid have been reacted with complimentary reactants to form larger polymers with the properties of telechelic precursors. Easily processable polyamide telechelics have not been available, and so likewise have the availability of polymers made from such polyamide telechelics, such as thermoplastic polyurethane (TPU) made from such polyamide telechelics.

[0020] Polymers such as TPU made from polyester polyols render good mechanical properties and UV and heat resistance, but they suffer from poor hydrolysis resistance. Polyether polyols have better hydrolytic stability than polyester polyols, but fall short in UV and heat resistance. Polycarbonate polyols offer improved hydrolysis and thermal resistance over polyester polyols with some degree of increased hardness, but they are an order of magnitude more expensive than other polyols. Polydiene polyols are useful but are too hydrophobic to interact well with polar substrates. Some polydiene polyols are hydrogenated to reduce degradation mechanisms relying on residual unsaturation from

the diene monomer. TPU made from any of these materials have generally poor adhesion to polar materials such as polyamides and polyesters. Therefore, a new class of telechelic polyamide will help overcome these problems and allow the preparation of polymers such as TPU that have improved overall properties.

[0021] Amine terminated polyamide oligomers were made with low viscosity, low glass transition temperature, suppressed crystallinity, low acid number, with various nitrogen or amide:hydrocarbon weight ratios (or hydrophilic/hydrophobic balance), with a controlled number of hydrogen bonding or non-hydrogen bonding amide groups. Polymers, and more specifically TPU, were made from the described amine terminated polyamide oligomers. The present invention is directed to these polymers.

[0022] The invention provides a polymer composition that includes the reaction product of: (i) a polyol component including the described telechelic polyamide; and (ii) a polyisocyanate component; and optionally (iii) a chain extender component.

The Polyisocyanate Component

[0023] The polyisocyanate component used to prepare the polymer compositions described herein includes an aliphatic polyisocyanate. Useful aliphatic polyisocyanates are not overly limited and may include any of the aliphatic polyisocyanate generally used in the preparation of TPU. In some embodiments the aliphatic polyisocyanate includes an aliphatic diisocyanate.

[0024] The polyisocyanate component may include one or more aliphatic polyisocyanates. In some embodiments the polyisocyanate component may also include an aromatic polyisocyanate but in such embodiments a majority of the polyisocyanate component is made up of aliphatic polyisocyanates.

[0025] In some embodiments the polyisocyanates are diisocyanates. Thus the polyisocyanate component may include one or more aliphatic diisocyanates. In some embodiments the polyisocyanate component may also include an aromatic diisocyanates but in such embodiments a majority of the polyisocyanate component is made up of aliphatic diisocyanates.

[0026] In some embodiments the polyisocyanate component is free of aromatic polyisocyanates. In some embodiments the polyisocyanate component is free of aromatic diisocyanates.

[0027] The use of multifunctional isocyanate compounds, i.e., triisocyanates, etc., which will cause crosslinking of the resulting polymer, are generally avoided in some embodiments and thus the amount used, if any, in such embodiments is generally less than 4 mole percent or even less than 2 mole percent based upon the total moles of all of the various isocyanates used.

[0028] Examples of suitable aliphatic diisocyanates include isophorone diisocyanate (IPDI), 1,4-cyclohexyl diisocyanate (CHDI), hexamethylene diisocyanate (HDI), 4,4'-methylene dicyclohexyl diisocyanate (H_{12} MDI), 1,6-diisocyanato-2,2,4,4-tetramethyl hexane (TMDI), 1,10-decane diisocyanate, trans-dicyclohexylmethane diisocyanate (HMDI), xylylene diisocyanate (XDI), m-tetramethyl xylylene diisocyanate (TMXDI), or any combination thereof. Commonly used diisocyanates are 4,4'-methylenebis(phenyl isocyanate) (MDI), hexamethylene diisocyanate (HDI), and 4,4'-methylene dicyclohexyl diisocyanate (H_{12} MDI). Dimers and trimers of the above diisocyanates may also be used as well as a blend of two or more diisocyanates.

[0029] In some embodiments the polyisocyanate component is 4,4'-methylenebis(phenyl isocyanate) (MDI). In some embodiments the polyisocyanate component is hexamethylene diisocyanate (HDI). In some embodiments the polyisocyanate component is 4,4'-methylene dicyclohexyl diisocyanate (H_{12} MDI).

[0030] The aliphatic polyisocyanate used in this invention may also be in the form of a low molecular weight polymer or oligomer which is end capped with an isocyanate. For example, a hydroxyl terminated polyester intermediate may be reacted with an isocyanate-containing compound to create a low molecular weight polymer end capped with isocyanate. In the TPU field, such materials are normally referred to as pre-polymers. Such pre-polymers normally have a number average molecular weight (Mn) which is within the range of about 500 to about 10,000 Daltons.

The Chain Extender Component

[0031] The optional chain extender component is not overly limited and may include any of the chain extenders generally used in the preparation of TPU.

[0032] Suitable chain extenders include lower aliphatic or short chain glycols having from about 2 to about 10 carbon atoms and include for instance ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, triethylene

glycol, cis-trans-isomers of cyclohexyl dimethylol, neopentyl glycol, 1,4-butanediol, 1,6-hexandiol, 1,3-butanediol, and 1,5-pentanediol. Aromatic glycols can also be used as the chain extender and are often the choice for high heat applications. Benzene glycol (HQEE) and xylylene glycols are suitable chain extenders for use in making the TPU of this invention. Xylylene glycol is a mixture of 1,4-di(hydroxymethyl) benzene and 1,2-di(hydroxymethyl) benzene. Benzene glycol is one suitable aromatic chain extender and specifically includes hydroquinone, i.e., bis(beta-hydroxyethyl) ether also known as 1,4-di(2-hydroxyethoxy) benzene; resorcinol, i.e., bis(beta-hydroxyethyl) ether also known as 1,3-di(2-hydroxyethyl) benzene; catechol, i.e., bis(beta-hydroxyethyl) ether also known as 1,2-di(2-hydroxyethoxy) benzene; and combinations thereof. In some embodiments, the chain extender is 1,4-butanediol.

[0033] Suitable chain extenders also include diamine chain extenders. Suitable diamine chain extenders can be aliphatic or aromatic in nature, such as alkylenediamines of from 1-30 carbon atoms (e.g., ethylenediamine, butanediamine, hexamethylenediamine).

[0034] In some embodiments the TPU of the invention are made using one or more chain extenders. In other embodiments the TPU of the invention are made without the use of any chain extenders.

The Polyol Component.

[0035] The polyol component used in the invention includes the described telechelic polyamide which are N-alkylated. They can be described as low molecular weight polyamide oligomers and telechelic polyamides (including copolymers) containing N-alkylated amide groups in the backbone structure.

[0036] The telechelic polyamides used in the invention are unique in that they may be liquid below about 70°C and can be reacted into other polymer networks to impart desirable properties. Many polyamides, e.g. the various nylon polymers, are insoluble solids at temperatures of about 80 to 260°C and thus would be difficult to homogenously react into other polymer networks. N-alkylating the nitrogen atom of the polyamide or the nitrogen bearing precursor of the polyamide disrupts some of the hydrogen bonding making the polyamide of this disclosure lower melting and more soluble.

[0037] The following terms have definitions as stated below: Telechelic polymers, defined as macromolecules that contain two reactive end groups and are used as cross-linkers, chain extenders, and important building blocks for various macromolecular structures, including block and graft copolymers, star, hyperbranched or dendritic polymers. Telechelic polymers of the polydiene, polyester, polyether, and polycarbonate type are well known in the art. These prior art telechelic polymers with functional end groups selected from primary or secondary hydroxyl, primary or secondary amine, and carboxylic acid have been reacted with complimentary reactants to form larger polymers with the properties of telechelic precursors. Easy to process polyamide telechelics with low melting points have not been available.

[0038] We will use the parentheses to designate 1) that the something is optionally present such that monomer(s) means monomer or monomers or (meth)acrylate means methacrylate or acrylate, 2) to qualify or further define a previously mentioned term, or 3) to list narrower embodiments.

[0039] Polyester polyols, and often TPU made from such polyols, render good mechanical properties and UV resistance, but they suffer from poor hydrolysis resistance. Polyether polyols, and resulting TPU, have better hydrolytic stability than polyesters, but fall short in UV resistance. Polycarbonate polyols, and resulting TPU, offer improved hydrolysis resistance over polyesters with some degree of increased hardness, but they are an order of magnitude more expensive than other polyols. Polydiene polyols are useful but are too hydrophobic to interact well with polar substrates. Some polydiene polyols are hydrogenated to reduce degradation mechanisms relying on residual unsaturation from the diene monomer. Therefore, a new class of telechelic polyamide will help overcome these problems.

[0040] Amine terminated polyamide oligomers have now been discovered which have low viscosity, low glass transition temperature, suppressed crystallinity, low acid number, with various nitrogen or amide:hydrocarbon weight ratios (or hydrophilic/hydrophobic balance), and with a controlled number of hydrogen bonding or non-hydrogen bonding amide groups.

[0041] A series of polyamide oligomers from conventional difunctional acids and amines were made. The initial oligomers contained amine terminations and in reaction with diisocyanates form polyamide-polyurea backbone. However, the presence of strong

hydrogen bond in these structures makes them very hard (high glass transition) even at low molecular-weight and therefore not suitable for further structural modifications or preparation higher molecular weight polymers or crosslinked networks. We discovered that substitution of N-alkyl groups on these polymers make then soft and easy to process.

[0042] This invention relates to TPU compositions prepared from these polyamide oligomers or telechelic polyamides, which are resistant to chain scission, e.g. by hydrolysis or UV degradation, useful as macromonomers, prepolymers or polymer segments to make higher molecular weight polymers and/or crosslinked polymer networks. The resulting TPU compositions have better thermal stability than similar polymers or networks from polyethers and/or polyesters due to the higher thermal stability of the amide bonds. Polymers built from moderate molecular weight polyamide oligomers and co-reactants that can form chemical bonds with co-reactive groups at the termini of the oligomers. These polymers have many of the properties of the polyamide oligomers from which they are made as the oligomers form a substantial weight percent of the final polymer. Modifying the molecular weight and composition of the oligomers can be used to achieve the desired properties. The composition may contain small amounts of other polymers and materials either as physical blends or where the other polymers or materials may be co-reacted into the polyamide.

[0043] The term polyamide oligomer will refer to an oligomer with two or more amide linkages, or sometimes the amount of amide linkages will be specified. A subset of polyamide oligomers will be telechelic polyamides. Telechelic polyamides will be polyamide oligomers with high percentages, or specified percentages, of two functional groups of a single chemical type, e.g. two terminal amine groups (meaning either primary, secondary, or mixtures), two terminal carboxyl groups, two terminal hydroxyl groups (again meaning primary, secondary, or mixtures), or two terminal isocyanate groups (meaning aliphatic , aromatic, or mixtures). Ranges for the percent difunctional that are preferred to meet the definition of telechelic are at least 70 or 80, more desirably at least 90 or 95 mole % of the oligomers being difunctional as opposed to higher or lower functionality. Reactive amine terminated telechelic polyamides will be telechelic polyamide oligomers where the terminal groups are both amine types, either primary or secondary and mixtures thereof, i.e. excluding tertiary amine groups.

[0044] The invention involves the use of the described polyamide oligomers or telechelic polyamides in the preparation of TPU compositions. The polyamide oligomers or telechelic polyamides may be used as the polyol component in the TPU forming reaction.

[0045] The invention includes the substitution of polyamide segments for polyester, polyether, or polycarbonate soft segments in telechelic oligomers. The replacement or substitution of polyamide segments for polyester, polyether, or polycarbonate segments can be partial or complete. Optimum environmental resistance, including thermal stability, would result from complete replacement of polyester and polyether segments, due to their potential for easier chain scission in polyethers and polyesters. In some embodiments some of the polyester and or polyether segments could be retained in the telechelic polyamide or polyamide oligomer for their ability to soften the elastomeric portion or modify the compatibility of the resulting polymer with other polymer surfaces. When polymer from polyesters or polyether are degraded by hydrolysis or UV activated chain scission the molecular weight of the polymer is decreased such that the polymer, or segment, soon loses its tensile strength, elongation to break, resistance to solvents, etc.

[0046] A second benefit of the invention, substituting soft polyamide segments for soft polyether or polyester segments, is that the polyamide segments tend to promote better wetting and adhesion to a variety of polar substrates, such as glass, nylon, and metals than polyester or polyether based polymers. The hydrophobic/hydrophilic nature of the polyamide can be adjusted by using different weight ratios of hydrocarbon to amide linkages, or nitrogen atoms, in the polyamide. Diacids, diamines, aminocarboxylic acids, and lactams with large aliphatic hydrocarbons portions relative to the amide linkage portion tend to be hydrophobic. When the hydrocarbon weight ratio to amide linkage, or nitrogen atoms, becomes smaller, the polyamide is more hydrophilic. Increasing the amount of polyamide in a polymer can increase adhesion to substrates that have similar or compatible surfaces to polyamides.

[0047] TPU made from described polyamide segments can have good solvent resistance. Solvents can cause deformation and swelling of a polymer thereby causing premature failure of the polymer. Solvents can cause a coating to swell and delaminate from a substrate at the interface between the two.

[0048] It should be noted that many of the polyamides of the prior art are high melting point crystalline polyamides such as 6-nylon, 6,6-nylon, 6,10-nylon that melt at temperatures much too high, e.g. in excess of 100°C, to serve as soft segments if a blocky thermoplastic polymer is desired. In some of the prior art publications the polyamide, often a crystalline or high Tg polyamide type, was added merely to increase the surface interaction with a substrate that was compatible to polyamides. To create a lower Tg polymer, soft (low Tg) polyester, polyether or polycarbonates were added to the polyamide segment to provide a lower composite Tg elastomeric segment. In other prior art publications only a few polyamide linkages were inserted into a polymer to modify the polarity of the polymer, to increase solvent resistance, or to raise the softening temperature.

[0049] One objective of the current patent application is to use high percentages of amide linkages in a telechelic oligomer comprised of one or more polyamide segments to provide resistance to chain scission from hydrolysis and/or UV activated chain scission. Thus many embodiments will describe soft segments with high percentages of total linkages between repeat units in the soft segment being amide linkages. Some embodiments may allow for some linkages between repeat units to be other than amide linkages.

[0050] An important modification from conventional polyamides to get low Tg polyamide soft segments is the use of monomers with secondary amine terminal groups in forming the polyamide. The amide linkage formed from a secondary amine and a carboxylic acid type group is called a tertiary amide linkage. Primary amines react with carboxylic acid type groups to form secondary amides. The nitrogen atom of a secondary amide has an attached hydrogen atom that often hydrogen bonds with a carbonyl group of a nearby amide. The intra-molecular H-bonds induce crystallinity with high melting point and can act as crosslinks reducing chain mobility. With tertiary amide groups the hydrogen on the nitrogen of the amide linkage is eliminated along with hydrogen bonding. A tertiary amide linkage that has one additional alkyl group attached to it as compared to a secondary amide group, which has hydrogen attached to it, has reduced polar interactions with nearby amide groups when the polymer exists in a bulk polymer sample. Reduced polar interactions mean that glassy or crystalline phases that include the amide linkage melt at lower temperatures than similar amide groups that are secondary

amide groups. One way to source secondary amine reactant, a precursor to tertiary amide linkages, is to substitute the nitrogen atom(s) of the amine containing monomer with an alkyl group. Another way to source a secondary amine reactant is to use a heterocyclic molecule where the nitrogen of the amine is part of the ring structure. Piperazine is a common cyclic diamine where both nitrogen atoms are of the secondary type and part of the heterocyclic ring.

[0051] Another modification to reduce the Tg of the polyamide soft segments is to use at least one additional monomer beyond the minimum number of monomers to form the polyamide. Thus for a polyamide formed from a lactam polymerization such as from N-methyl-dodecyl lactam one would include an additional lactam, aminocarboxylic acid, diamine, or dicarboxylic acid in the monomers for the polymerization to change the spacing (among repeat units) between the amide linkages formed by the monomer so that the spacing between the amide linkages in the polyamide is irregular along the backbone, e.g. not the same physical dimension for some of the repeat units in each oligomer. For a polymerization of aminocarboxylic acid one would include additional lactam, aminocarboxylic acid, diamine, or dicarboxylic acid (with different physical length between the primary reactive groups of the monomer) in the monomer blend for the polymerization to change the spacing among repeat units between the amide linkages. Switching end groups on the monomers can also disrupt regularity in the spacing of the polar amide linkages and lower the effective Tg of the copolymer. Thus co-polymerizing a C_6 amino carboxylic acid with a small portion of a C_6 diacid and C_6 diamine can disrupt regularity of the amide linkages as the diacid and diamine units would switch the orientation of the amide linkage from head to tail orientation to tail to head orientation, slightly disrupting uniformity of spacing of the amide linkages along the polyamide backbone. Typically when following this procedure one would try to add a disrupting monomer that increased or decreased the number of atoms between the amide forming end groups of the monomer(s) used as the primary monomer in the polyamide. One could also use a second disrupting monomer that had a cyclic structure, such as piperazine, a cyclic diamine monomer where two methylene atoms form the top half of the ring and two methylene atoms form the bottom half of the ring, to disrupt the regularity of polyamide formed from a diacid reacted with a diamine monomer with two methylene atoms between the nitrogen atoms of the diamine.

[0052] Another way to express the use of a copolymerization method to reduce the Tg and consequently the hardness of the polyamide is that the polyamide is characterized as being within (a), (b) or (c): (a) when said amide linkages are derived from polymerizing one or more monomers and more than 90 mole percent of said monomers are derived from polymerizing monomers selected from lactam and aminocarboxylic acid monomer then said polyamide is defined as a copolymer of at least two different monomers (meaning said monomers are characterized as being at least two different monomers because they have hydrocarbyl portion of different spacing length between the amine and carboxylic acid groups, wherein each of said at least two different monomers is present at molar concentrations of at least 10%, more desirably at least 20 or 30% of the total lactam and/or aminocarboxylic acid monomers in said polyamide); or (b) when said amide linkages are derived from polymerizing two or more monomers and more than 90 mole percent of said monomers were derived from polymerizing dicarboxylic acid and diamine monomers then said polyamide is defined as a terpolymer of at least three different monomers (meaning said amide linkages are formed from at least three different monomers selected from the group of dicarboxylic acid and diamine monomers wherein said at least three different monomers are characterized as different from each other by a hydrocarbyl group of different spacing length between the carboxylic acid groups of the dicarboxylic acid, or different spacing length between the amine groups of the diamine, wherein each of said at least three different monomers is present at concentrations of at least 10 mole %, more desirably at least 20 or 30 mole percent, of the total monomers in said polyamide); or (c) with the proviso that if said amide linkages are derived from polymerizing a combination of dicarboxylic acid, diamine and either lactam and/or aminocarboxylic acid monomers such that the total dicarboxylic acid monomer(s) and the diamine monomer(s) are present in the monomer blend at concentrations of at least 10 mole percent, more desirably at least 20 or 30 mole percent, and the total lactam and aminocarboxylic acid monomers are present in the monomer blend at concentrations of at least 10 mole %, more desirably at least 20 or 30 mole percent, then there are no restrictions requiring additional different monomers.

[0053] Generally having nearly equal amounts of two or more different amide forming monomers results in different spacing between the amide linkages along the polyamide backbone and affords optimal reduction of the crystalline melting and glass

transition temperatures. For example, a 50:50 mole blend of two different diamines would be desirable. A 50:50 mole blend of two different diacids would be desirable. A 33:33;33 mole blend of a lactam with a diacid and a diamine would be desirable.

[0054] We use the term low Tg, glass transition temperature, even though we realize most of the polyamide segments are initially low molecular weight and it would not be easily possible to measure the Tg of the low molecular weight oligomers, the measured value would be dramatically affected by molecular weight. High Tg polymers, e.g. having Tg values above 70, 80, or 90°C as measured by differential scanning calorimetry (DSC), would tend to form solids or gels even at low molecular weights. Thus the polyamide oligomers, telechelic polyamides, and even the oligomers from telechelic polyamides or polyamide oligomers are often described in this specification by their viscosity at specific temperatures. Low Tg polyamides oligomers will be defined as those compositions that would have Tg, if above 20,000 g/mole molecular weight, of below 50°C, more desirably below 25 or 0°C.

[0055] In one embodiment the telechelic oligomer or telechelic polyamide will have a viscosity measured by a Brookfield circular disc viscometer with the circular disc spinning at 5 rpm of less than 100,000 cps at a temperature of 70°C, more desirably less than 15,000 or 10,000 cps at 70°C, still more desirably less than 100,000 cps at 60 or 50°C, and more preferably less than 15,000 or 10,000 cps at 60°C; and still more preferable less that 15,000 or 10,000 cps at 50°C. Desirably these viscosities are those of neat telechelic prepolymers or polyamide oligomers without solvent or plasticizers. These viscosity values will facilitate mixing the telechelic polyamide with co-reactants and or particulate materials under suitable conditions that desirable reactions occur at reasonable rates and undesirable reactions, e.g. side reactions, do not occur to any significant extent. In some embodiments the telechelic polyamide can be diluted with solvent to achieve viscosities in these ranges.

[0056] Many of the oligomers, telechelics, and polymers of this specification are made by condensation reactions of reactive groups on desired monomer(s). Lactam polymerization into a polyamide results in similar amide linkages by a chain polymerization process and is well known in the art. These condensation reactions between carboxylic acid groups and amine or hydroxyl groups are well known and are driven by the removal of water and or catalysts. The formation of amides from the

reaction of carboxylic acid groups and amine groups can be catalyzed by boric acid, boric acid esters, boranes, phosphorous acid, phosphates, phosphate esters, amines, acids, bases, silicates, and silsesquioxanes. Additional catalysts, conditions, etc. are available in textbooks such as "Comprehensive Organic Transformations" by Larock.

[0057] The condensation reaction of reactive groups will be defined as creating chemical linkages between the monomers. The portion of the monomer that is incorporated into the oligomer or polymer will be defined as the repeat unit from the particular monomer. Some monomers, such as aminocarboxylic acid, or one end of diacid reacting with one end of a diamine, lose one molecule of water as the monomer goes from a monomer to a repeat unit of a polymer. Other monomers, such as lactams, isocyanates, amines reacted with isocyanates, hydroxyl groups reacted with isocyanates, etc. do not release a portion of the molecule to the environment but rather retain all of the monomer in the resulting polymer.

[0058] We will define polyamide oligomer as a species below 20,000 g/mole molecular weight, e.g. often below 10,000; 5,000; 2,500; or 2000 g/mole, that has two or more amide linkages per oligomer. Later we will define preferred percentages of amide linkages or monomers that provide on average one amide linkage per repeat unit in various oligomeric species. A subset of polyamide oligomer will be telechelic oligomer. The telechelic polyamide has molecular weight preferences identical to the polyamide oligomer above. The term telechelic has been earlier defined. Multiple polyamide oligomers or telechelic polyamides can be linked with condensation reactions to form polymers, generally above 100,000 g/mole.

[0059] Generally amide linkages are formed from the reaction of a carboxylic acid group with an amine group or the ring opening polymerization of a lactam, e.g. where an amide linkage in a ring structure is converted to an amide linkage in a polymer. In a preferred embodiment a large portion of the amine groups of the monomers are secondary amine groups or the nitrogen of the lactam is a tertiary amide group. Secondary amine groups form tertiary amide groups when the amine group reacts with carboxylic acid to form an amide. For the purposes of this disclosure the carbonyl group of an amide, e.g. as in a lactam, will be considered as derived from a carboxylic acid group. The amide linkage of a lactam is formed from the reaction of carboxylic group of an aminocarboxylic acid with the amine group of the same aminocarboxylic acid. In one

embodiment we want less than 20, 10 or 5 mole percent of the monomers used in making the polyamide to have functionality in polymerization of amide linkages of 3 or more. This will reduce branching in the polyamide oligomer or telechelic polyamide.

[0060] The polyamide oligomers and telechelic polyamides of this disclosure can contain small amounts of ester linkages, ether linkages, urethane linkages, urea linkages, etc. if the additional monomers used to form these linkages are useful to the intended use of the polymers. This allows other monomers and oligomers to be included in the polyamide to provide specific properties, which might be necessary and not achievable with a 100% polyamide segment oligomer. Sometimes added polyether, polyester, or polycarbonate provides softer e.g. lower Tg, segments. Sometimes it is desirable to convert the carboxylic end groups or primary or secondary amine end groups of a polyamide to other functional end groups capable of condensation polymerizations. A telechelic polyamide with carboxylic end groups can be converted into an oligomer with hydroxyl end groups by reacting the telechelic polyamide with a polyether that has two hydroxyl end groups or a polyether that has one amino, primary or secondary, and one hydroxyl end group. Oligomers or polymers with polyether segments have susceptibility to chain breakage due to UV exposure. The effect of UV exposure on block copolymers of nylon 6-polyethylene glycol block copolymers is reported in Gauvin, Pascal; Lemaire, Jacques in Makromolekulare Chemie (1987), 188(5), 971-986. Sometimes an initiator for oligomer chain polymerization of a lactam is used that doesn't generate an amide linkage. Sometimes a polyether might be used as a segment or portion of a polyamide to reduce the Tg, or provide a soft segment, of the resulting polyamide oligomer. Sometimes a polyamide segment, e.g. possibly difunctional with carboxylic acid or amine terminal groups, can be functionalized with two polyether end segments (such as from Jeffamine™ D230) to further lower the Tg of, or provide a soft segment in, the polyamide oligomer and create a telechelic polyamide with amine or hydroxyl end groups. Sometimes a carboxylic acid terminated telechelic polyamide segment is functionalized by reacting with an amino alcohol, e.g. N-methylaminoethanol, which can create a telechelic polyamide with terminal hydroxyl groups. In one embodiment the functional primary or secondary amine groups of a telechelic polyamide are reacted with a lactone of 2, 3 or 4 to 10 carbon atoms (e.g. a , butyro-, valero-, or caprolactone) and/or hydroxyl carboxylic acid of 3 to 30 carbon atoms to create one or two hydroxyl

functional end groups derived from said lactone or said hydroxyl carboxylic acid on said telechelic polyamide. Optimally only one repeat unit from said lactone or hydroxyl carboxylic acid is added to each end of said telechelic polyamide.

[0061] As earlier indicated many amide forming monomers create on average one amide linkage per repeat unit. These include diacids and diamines when reacted with each other, aminocarboxylic acids, and lactams. These monomers, when reacted with other monomers in the same group, also create amide linkages at both ends of the repeat units formed. Thus we will use both percentages of amide linkages and mole percent and weight percentages of repeat units from amide forming monomers. Amide forming monomers will be used to refer to monomers that form on average one amide linkage per repeat unit in normal amide forming condensation linking reactions.

[0062] In one embodiment desirably at least 10 mole percent, more desirable at least 25, 45 or 50, and still more desirably at least 60, 70, 80, 90, or 95 mole % of the total number of the heteroatom containing linkages connecting hydrocarbon type linkages are characterized as being amide linkages. Heteroatom linkages are linkages such amide, ester, urethane, urea, ether linkages where a heteroatom connects two portions of an oligomer or polymer that are generally characterized as hydrocarbons (or having carbon to carbon bond, such as hydrocarbon linkages). As the amount of amide linkages in the polyamide increase the amount of repeat units from amide forming monomers in the polyamide increases.

~~[0063]~~ In one embodiment desirably at least 25 wt. %, more desirable at least 30, 40, 50, more desirably at least 60, 70, 80, 90, or 95 wt. % of the polyamide oligomer or telechelic polyamide is repeat units from amide forming monomers, also identified as monomers that form amide linkages at both ends of the repeat unit. Such monomers include lactams, aminocarboxylic acids, dicarboxylic acid and diamines.

[0064] In one embodiment desirably at least 50, 65, 75, 76, 80, 90, or 95 mole percent of the amide linkages in the polyamide oligomer or telechelic polyamine are tertiary amide linkages. As earlier explained tertiary amide linkages result from ring opening polymerization of lactams with tertiary amides or reactions of secondary amines with carboxylic acid groups.

[0065] The percent of tertiary amide linkages of the total number of amide linkages was calculated with the following equation:

$$Tertiary\ amide\ linkage\ \% = \frac{\sum_{i=1}^{n}(w_{tertN,i} \times n_i)}{\sum_{i=1}^{n}(w_{totalN,i} \times n_i))} \times 100$$

where: n is the number of monomers; the index i refers to a certain monomer; w_{tertN} is the average number nitrogen atoms in a monomer that form or are part of tertiary amide linkages in the polymerizations, (note: end-group forming amines do not form amide groups during the polymerizations and their amounts are excluded from w_{tertN}); w_{totalN} is the average number nitrogen atoms in a monomer that form or are part of tertiary amide linkages in the polymerizations (note: the end-group forming amines do not form amide groups during the polymerizations and their amounts are excluded from w_{totalN}); and n_i is the number of moles of the monomer with the index i.

[0066] The percent of amide linkages of the total number of all heteroatom containing linkages (connecting hydrocarbon linkages) was calculated by the following equation:

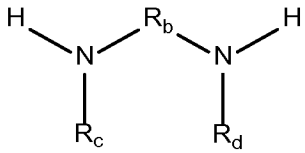
$$Amide\ linkage\ \% = \frac{\sum_{i=1}^{n}(w_{totalN,i} \times n_i)}{\sum_{i=1}^{n}(w_{totalS,i} \times n_i)} \times 100$$

where: w_{totalS} is the sum of the average number of heteroatom containing linkages (connecting hydrocarbon linkages) in a monomer and the number of heteroatom containing linkages (connecting hydrocarbon linkages) forming from that monomer by the reaction with a carboxylic acid bearing monomer during the polyamide polymerizations; and all other variables are as defined above. The term "hydrocarbon linkages" as used herein are just the hydrocarbon portion of each repeat unit formed from continuous carbon to carbon bonds (i.e. without heteroatoms such as nitrogen or oxygen) in a repeat unit. This hydrocarbon portion would be the ethylene or propylene portion of ethylene oxide or propylene oxide; the undecyl group of dodecyllactam, the ethylene group of ethylenediamine, and the $(CH_2)_4$ (or butylene) group of adipic acid.

[0067] Preferred amide or tertiary amide forming monomers include dicarboxylic acids, diamines, aminocarboxylic acids and lactams. Preferred dicarboxylic acids are where the alkylene portion of the dicarboxylic acid is a cyclic, linear, or branched (optionally including aromatic groups) alkylene of 2 to 36 carbon atoms, optionally including up to 1 heteroatom per 3 or 10 carbon atoms of the diacid, more preferably from 4 to 36 carbon atoms (the diacid would include 2 more carbon atoms than the

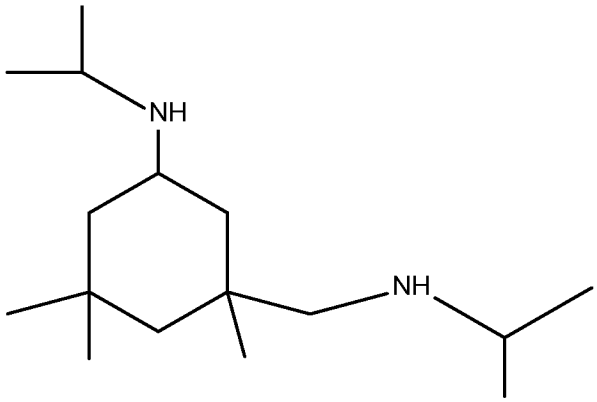
alkylene portion). These include dimer fatty acids, hydrogenated dimer acid, sebacic acid, etc. Generally we prefer diacids with larger alkylene groups as this generally provides polyamide repeat units with lower Tg value.

[0068] Preferred diamines include those with up to 60 carbon atoms, optionally including one heteroatom (besides the two nitrogen atoms) for each 3 or 10 carbon atoms of the diamine and optionally including a variety of cyclic, aromatic or heterocyclic groups providing that one or both of the amine groups are secondary amines, a preferred formula is:

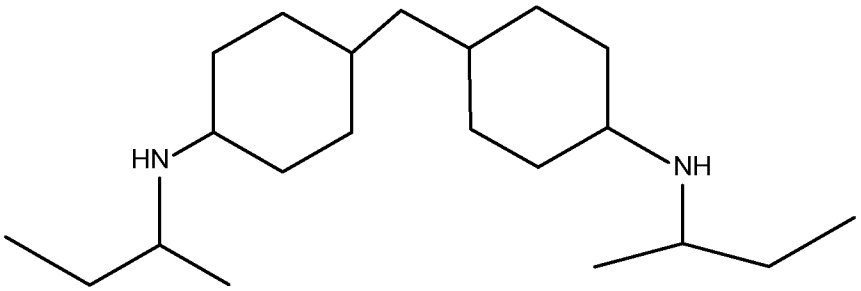


wherein: R_b is a direct bond or a linear or branched (optionally being or including cyclic, heterocyclic, or aromatic portion(s)) alkylene group (optionally containing up to 1 or 3 heteroatoms per 10 carbon atoms of the diamine) of 2 to 36 carbon atoms and more preferably 2 or 4 to 12 carbon atoms; and R_c and R_d are individually a linear or branched alkyl group of 1 to 8 carbon atoms, more preferably 1 or 2 to 4 carbon atoms or R_c and R_d connect together to form a single linear or branched alkylene group of 1 to 8 carbon atoms or optionally with one of R_c and R_d is connected to R_b at a carbon atom, more desirably R_c and R_d being 1 or 2 to 4 carbon atoms.

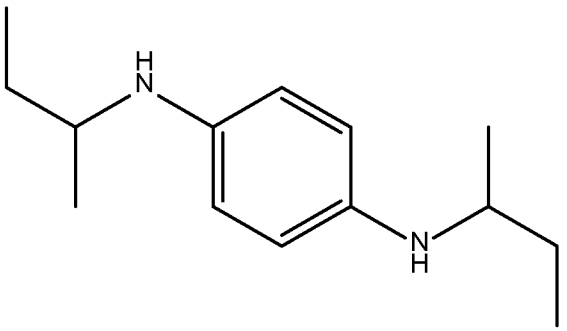
[0069] Such diamines include Ethacure™ 90 from Albermarle (supposedly a N,N'-bis(1,2,2-trimethylpropyl)- 1,6-hexanediamine); Clearlink™ 1000 from Dorfketal, or Jefflink™ 754 from Huntsman; N-methylaminoethanol; dihydroxy terminated, hydroxyl and amine terminated or diamine terminated poly(alkyleneoxide) where the alkylene has from 2 to 4 carbon atoms and having molecular weights from about 40 or 100 to 2000; N,N'-diisopropyl-1,6-hexanediamine; N,N'-di(sec-butyl) phenylenediamine; piperazine;, homopiperazine; and methyl-piperazine. Jefflink™754 has the structure:



while Clearlink™ 1000 has the structure:



while another diamine with an aromatic group is: N,N'-di(sec-butyl) phenylenediamine, see structure below:

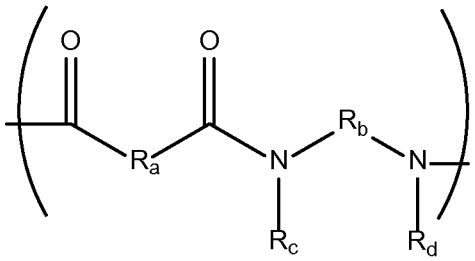


where preferred diamines are diamines wherein both amine groups are secondary amines.

[0070] Preferred lactams are lactams include straight chain or branched alkylene segments therein of 4 to 12 carbon atoms such that the ring structure without substituents on the nitrogen of the lactam has 5 to 13 carbon atoms total (when one includes the carbonyl) and the substituent on the nitrogen of the lactam (if the lactam is a tertiary amide) is an alkyl group of from 1 to 8 carbon atoms and more desirably an alkyl group of 1 to 4 carbon atoms. Dodecyl lactam, alkyl substituted dodecyl lactam, caprolactam, alkyl substituted caprolactam, and other lactams with larger alkylene groups are

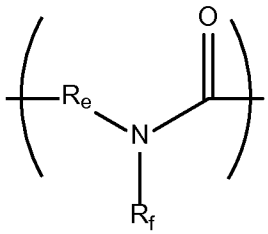
preferred lactams as they provide repeat units with lower Tg values. Aminocarboxylic acids have the same number of carbon atoms as the lactams. Desirably the number of carbon atoms in the linear or branched alkylene group between the amine and carboxylic acid group of the aminocarboxylic acid is from 4 to 12 and the substituent on the nitrogen of the amine group (if it is a secondary amine group) is an alkyl group with from 1 to 8 carbon atoms, more preferably 1 or 2 to 4 carbon atoms. Aminocarboxylic acids with secondary amine groups are preferred.

[0071] In one embodiment desirably at least 50 wt. %, more desirably at least 60, 70, 80 or 90 wt. % of said polyamide oligomer or telechelic polyamide comprise repeat units from diacids and diamines of the structure of the repeat unit being:



wherein: R_a is the alkylene portion of the dicarboxylic acid and is a cyclic, linear, or branched (optionally including aromatic groups) alkylene of 2 to 36 carbon atoms, optionally including up to 1 heteroatom per 3 or 10 carbon atoms of the diacid, more preferably from 4 to 36 carbon atoms (the diacid would include 2 more carbon atoms than the alkylene portion); and R_b is a direct bond or a linear or branched (optionally being or including cyclic, heterocyclic, or aromatic portion(s)) alkylene group (optionally containing up to 1 or 3 heteroatoms per 10 carbon atoms) of 2 to 36 or 60 carbon atoms and more preferably 2 or 4 to 12 carbon atoms and R_c and R_d are individually a linear or branched alkyl group of 1 to 8 carbon atoms, more preferably 1 or 2 to 4 carbon atoms or R_c and R_d connect together to form a single linear or branched alkylene group of 1 to 8 carbon atoms or optionally with one of R_c and R_d is connected to R_b at a carbon atom, more desirably R_c and R_d being an alkyl group of 1 or 2 to 4 carbon atoms.

[0072] In one embodiment desirably at least 50 wt. %, more desirably at least 60, 70, 80 or 90 wt. % of said polyamide oligomer or telechelic polyamide comprise repeat units from lactams or amino carboxylic acids of the structure:



Repeat units can be in a variety of orientations in the oligomer derived from lactams or amino carboxylic acid depending on initiator type, wherein each R_e independently is linear or branched alkylene of 4 to 12 carbon atoms and each R_f independently is a linear or branched alkyl of 1 to 8, more desirably 1 or 2 to 4, carbon atoms.

[0073] The above described polyamide oligomers and telechelic polyamide are useful to make polymers by reacting the polyamide oligomer or telechelic polyamide with co-reactants having two or more reactive groups that can form chemical bonds when reacted with the functional groups of the polyamide oligomers or telechelic polyamide (e.g. these functional groups of the polyamide include primary and secondary amine, primary or secondary hydroxyl, or carboxylic acid group). The reactive groups on the co-reactants may be isocyanate, or with particular telechelic polyamides they could be hydroxyl, amine or carboxylic acid groups.

[0074] While not wishing to be bound by theory, it is believed the telechelic polyamides described herein are uniquely suited for use in the preparation of polymers, including TPU. This is mainly due to their viscometric properties and their relatively low glass transition temperatures. These properties make the telechelic polyamides described herein much easier to use and handle at conditions generally used for the preparation of polymers like TPU thus overcoming a significant barrier to use polyamide materials that has previously made it difficult to effectively prepare TPU using polyamide materials.

[0075] The polymers of the invention may also be blended with one or more conventional polymers. For example, one or more polymers of the invention may be physically blended with a polyester TPU, a polyether TPU, a polycarbonate TPU, or any combination thereof.

[0076] The weight average molecular weight (Mw) of the polymers of the invention can range from 80,000 to 600,000 g/mol, or from 100,000 to 300,000, or from 80,000 to about 250,000 g/mol. The Mw of the polymer is measured according to gel permeation chromatography (GPC) against polystyrene standard.

[0077] The TPU polymers of the present invention can be mixed with various conventional additives or compounding agents, such as fillers, antioxidants, antiozone agents, antihydrolysis agents, extrusion aids, UV stabilizers, chain terminators, light stabilizers, colorants, extenders, pigments, lubricants, plasticizers, flame retardants, UV absorbers, and the like. Fillers that can be used include talc, silicates, clays, calcium carbonate, and the like. The level of additives will depend on the final properties and cost of the desired end-use application, as is well known to those skilled in the art of compounding TPUs. The additives may be added during the reaction to form the TPU, or in a second compounding step.

[0078] Antioxidants typically prevent or terminate oxidation reactions that result in degradation of the polyurethane article over the lifetime of the article. Typical antioxidants include ketones, aldehydes, and aryl amines, as well as phenolic compounds. Specific examples of compounds include ethylenebis(oxyethylene)bis(3-t-butyl-4-hydroxy-5-methylcinnamate and tetrakis-[methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane. Examples of suitable commercial antioxidants include Irganox 1010, Irganox 1098, Irganox 565, and Irganox 1035 (Ciba-Geigy Corp., Ardsley, N.Y.).

[0079] Antiozone agents prevent or reduce damage caused by ozone and antihydrolysis agents prevent or reduce damage by water and other hydrolyzing compounds. Examples of suitable antiozonants include p-phenylenediamine derivatives. Antihydrolysis agents include, for example, Stabaxol P and Stabaxol P-200 (Rhein Chemie, Trenton, N.J.).

[0080] Extrusion aids facilitate movement of the polyurethane through the extruder. Waxes, such as Wax E (Hoechst-Celanese Corp., Chatham, N.J.), Acrawax (Lonza Inc., Fair Lawn, N.J.) and oxidized polyethylene 629A (Allied-Signal Inc., Morristown, N.J.), are suitable extrusion aids. These extrusion aids can also act as mold-release agents or additional mold release agents can be added to the composition.

[0081] Chain terminators are used to control molecular weight. Examples of chain terminators include monoalcohol compounds having 8 or more carbon atoms.

[0082] Light stabilizers prevent or reduce degradation of a polymer product due to visible or ultraviolet light. Examples of suitable light stabilizers include benzotriazole, such as Tinuvin P, and hindered amine light stabilizers, such as Tinuvin 770.

[0083] Generally speaking, the compositions of the invention are focused thermoplastic polyurethanes. In some embodiments, the compositions of the invention are essentially free of and even free of thermoset polyurethanes, that is materials that cannot be re-melted or re-worked, for example due to significant crosslinking or similar reaction that is a feature of thermoset materials.

[0084] The polymers of the invention are specifically suited for a group of applications where conventional polymers, and more specifically conventional TPU, do not have the necessary level of solvent resistance, hydrolytic stability, oxidative stability, thermal stability, and/or adhesion to polar materials. These applications include injection molded articles, articles of automotive exterior, electronic components, extruded films, or combinations thereof.

[0085] In some embodiments the polymer compositions described herein are used to make injection molded articles. In some embodiments the polymer compositions described herein are used to make articles of automotive exterior. In some embodiments the polymer compositions described herein are used to make electronic components. In some embodiments the polymer compositions described herein are used to make extruded films. The polymer compositions described herein have shown themselves to have a balance of properties exceptionally well suited for these end us applications and/or methods of processing.

[0086] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention.

EXAMPLES

[0087] The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate the invention, they are not intended to limit it.

[0088] A set of aliphatic thermoplastic polyurethanes (TPU) are prepared that include several inventive examples made using hexamethylene diisocyanate (HDI), which may also referred to as 1,6-hexanediisocyanate, and the polyol components comprising a telechelic polyamides described herein. These TPU are compared to similar

materials made using standard commercial polyols to evaluate differences in various properties including higher heat resistance.

[0089] The TPU examples are prepared by reacting the polyol component, the polyisocyanate, and when present the chain extender component, under reaction conditions. A tin catalyst is used in 40 ppm. The hard segment of the TPU compositions varies from 18% to 40% in order to produce TPU of varying hardness for more proper comparisons.

[0090] The examples use the following polyol components: (i) a polyol component comprising a telechelic polyamide prepared from sebacic and dodecanedioic acids, piperazine and polytetramethylene oxide (PTMO) having a weight average molecular eight of about 1600, referred to as A-POLYOL A; (ii) a polyol component comprising a telechelic polyamide prepared from sebacic acid, piperazine and PTMO having a weight average molecular weight of about 2600, referred to as A-POLYOL B; (ii) a polyol component comprising a telechelic polyamide prepared from sebacic acid, piperazine and PTMO having a weight average molecular weight of about 2100, referred to as A-POLYOL C; (iv) a polyol component comprising a telechelic polyamide prepared from sebacic acid, piperazine and PTMO having a weight average molecular weight of about 3100, referred to as A-POLYOL D; (v) a polyol component comprising a telechelic polyamide prepared from sebacic acid, piperazine and PTMO having a weight average molecular weight of about 4100, referred to as AMIDE POLYOL E; and then for the comparative materials (v) a polycaprolactone polyester polyol having a weight average molecular weight of about 2000, referred to as POLYOL F; (vi) a polytetramethylene glycol polyether polyol having a weigh average molecular weight of about 1000, referred to as POLYOL G; and (vii) a linear, hydroxyl-terminated, aliphatic polycarbonate having a weigh average molecular weight of about 2000, commercially available from Bayer as Desmophen™ C2200, referred to as POLYOL H.

[0091] The examples use the following polyisocyanate components: (i) hexamethylene diisocyanate (HDI); and for a comparative material, diphenyl methane-4, 4'-diisocyanate (MDI).

[0092] All of the examples use 1,4-butanediol (BDO) as the chain extender.

[0093] The Examples are summarized in the table below.

Table 1: Summary of Examples

Ex. No.	Polyol	Polyisocyanate	Chain Extender	% Hard Segment
1.1	A-POLYOL A	HDI	BDO	39.6
1.2	A-POLYOL A	HDI	BDO	33.0
1.3	A-POLYOL A	HDI	BDO	27.7
1.4	A-POLYOL A	HDI	BDO	21.2
2.1	A-POLYOL A	HDI	BDO	24.0
3.1	A-POLYOL B	HDI	BDO	25.0
3.2	A-POLYOL C	HDI	BDO	21.6
3.3	A-POLYOL D	HDI	BDO	24.4
3.4	A-POLYOL E	HDI	BDO	15.8
Ref 1	A-POLYOL A	MDI	BDO	38.3
Ref 2	POLYOL F	HDI	BDO	17.1
Ref 3	POLYOL G	HDI	BDO	23.1
Ref 4	POLYOL H	HDI	BDO	17.1

[0094] The thermal resistance of each example is evaluated by a method developed by the present inventors using a dynamic mechanical analyzer and determining the temperature at which tan delta equals 1 at 1Hz frequency. The higher the value reported where tan delta equals 1 the better the samples thermal resistance. Sample characterization also includes determination of Shore hardness by ASTM D 2240, tensile and elongation characteristics by ASTM D412, and abrasion loss by ISO 4649. Haze is measured in 2mm thick plaques with a digital hazemeter (BYK Haze-gard plus) where a lower value indicates a better result. GPC is measured in NMP solution against PS standards. The table below summarizes key results and includes comparisons.

Table 2: Summary of Results

Ex. No.	Tensile Strength (N/mm^2)	M100% (N/mm^2)	M300% (N/mm^2)	Elonga-tion (%)	Shore A Hardness	Tan Delta Peak	Tan Delta = 1	Haze
1.1	35.1	9.2	20.6	425	93.8	-13.0	187.6	18.8
1.2	34.6	9.1	16.0	581	91.1	-14.9	174.5	18.2
1.3	37.0	11.0	11.0	600	89.1	-16.0	159.3	14.4
1.4	33.1	6.6	6.6	610	82.9	-21.8	144.9	11.2
2.1	22.9	7.1	16.3	587	86.9	-15.7	155.8	6.3
3.1	23.0	5.3	8.4	783	86.8	-37.3	174.9	8.2
3.2	112.4	180.7	70.8	12.7	84.1	-42.1	163.9	10.7
3.3	119.7	185.7	126.9	17.8	85.9	-40.0	167.1	12.5
3.4	120.8	183.9	74.8	15.8	82.6	-37.3	191.8	12.7
Ref 1					84.0			
Ref 2	20.2	4.0	6.9	708	86.7	-27.5	132.3	25.6
Ref 3	17.6	3.9	6.0	908	86.8	-45.7	121.8	16.0
Ref 4	38.0	4.1	11.1	636	84.5	-18.2	140.0	19.4

[0095] Additional properties are tested for some of the samples. Density is determined by ASTM D-792. Weatherability is measured by keeping the molded samples in a climatic chamber at 80°C and 95%RH for several weeks, and then measuring tensile strength retention determined by ASTM D412 where higher retention of physical properties indicate better weatherability properties. UV resistance is evaluated by a method developed by the present inventors using a xenotest instrument and UV-A, 10h, 80°C, 550W conditions, and yellow index (YI) is measured before and after the exposure, where lower values and smaller changes indicated better UV resistance. The table below summarizes results collected with blank fields indicating the data was note collected for the that test for that example.

Table 3: Summary of Additional Results

Ex. No.	Density	Weather; after 1 week	Weather; after 2 weeks	Weather; after 3 weeks	UV; initial YI	UV; final YI
1.1						
1.2						
1.3						
1.4						
2.1	1.08	103	78	60	56.4	40.9
3.1	1.07	95	79		13.8	12.4
3.2						
3.3						
3.4						
Ref 1					63.5	79.2
Ref 2	1.15	75	40	0		
Ref 3	1.04	93	103	89		
Ref 4	1.14	89	101	107		

[0096] The results show that the aromatic polymer compositions of the present invention provide a unique combination of properties that make them very well suited for applications that require strong physical properties and good thermal resistances, as well as optionally good weatherability and/or UV resistance. These combinations of properties are not present in other similar polymer compositions, as demonstrated by the reference examples provided above.

[0097] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise indicated, all numerical quantities in this description specifying amounts, reaction conditions, molecular weights, number of

carbon atoms, etc., are to be understood as modified by the word "about." Unless otherwise indicated, all percent and formulation values are on a molar basis. Unless otherwise indicated, all molecular weights are number average molecular weights. Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration. All of the embodiments of the invention described herein are contemplated from and may be read from both an open-ended and inclusive view (i.e. using “comprising of” language) and a closed and exclusive view (i.e. using “consisting of” language). As used herein parentheses are used designate 1) that the something is optionally present such that monomer(s) means monomer or monomers or (meth)acrylate means methacrylate or acrylate, 2) to qualify or further define a previously mentioned term, or 3) to list narrower embodiments.

What is claimed is:

1. A polymer composition comprising the reaction product of: (i) a polyol component comprising a telechelic polyamide; and (ii) an aliphatic polyisocyanate component; and optionally (iii) a chain extender component;

wherein the telechelic polyamide:

a) has repeat units derived from polymerizing monomers connected by linkages between the repeat units and functional end groups selected from carboxyl or primary or secondary amine, wherein at least 70 mole percent of telechelic polyamide have exactly two functional end groups of the same functional type selected from the group consisting of amino or carboxylic end groups;

b) has a polyamide segment comprising at least two amide linkages characterized as being derived from reacting an amine with a carboxyl group, and said polyamide segment comprising repeat units derived from polymerizing two or more of monomers selected from lactams, aminocarboxylic acids, dicarboxylic acids, and diamines;

c) wherein at least 10 percent of the total number of the heteroatom containing linkages connecting hydrocarbon type linkages are characterized as being amide linkages; and

d) wherein at least 25 percent of the amide linkages are characterized as being tertiary amide linkages.

2. The polymer composition of claim 1 wherein said polyamide segment of feature (b) is characterized as meeting at least one of the following conditions:

(i) where said amide linkages are derived from polymerizing amide forming monomers and at least 90 mole percent of said monomers are selected from the group consisting of lactams and aminocarboxylic acid monomers such that said polyamide is a copolymer of at least two different monomers; or

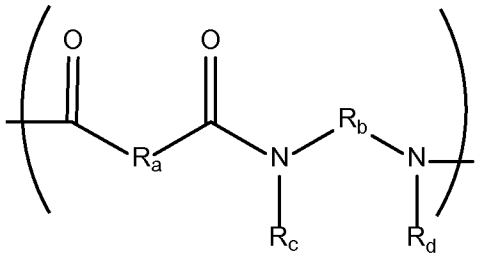
(ii) where said amide linkages are derived from polymerizing amide forming monomers and at least 90 mole percent of said monomers are combined amounts of dicarboxylic acid and diamine monomers such that said polyamide is a terpolymer of at least three different monomers; or

(iii) where said amide linkages are derived from polymerizing a combination of dicarboxylic acid, diamine and either lactam and/or aminocarboxylic acid monomers such that the total dicarboxylic acid monomer(s) and the diamine monomer(s) are present at 10 mole percent or more and the total lactam and/or aminocarboxylic acid monomers are present in the monomer blend at 10 mole percent or more.

3. The polymer composition of any of the claims 1 to 2 wherein at least 50 weight percent of said telechelic polyamide is made up of repeating units derived from monomers selected from the group of lactam monomers, aminocarboxylic acid monomers, dicarboxylic acid monomers, and diamine monomers.

4. The polymer composition of any of the claims 1 to 3 wherein at least 10 weight percent of said polymer is made up of repeating units derived from monomers selected from the group of lactam monomers, aminocarboxylic acid monomers, dicarboxylic acid monomers, and diamine monomers.

5. The polymer composition of any of the claims 1 to 4 wherein at least 50 weight percent of said polyamide segment comprises repeat units of the structure:



wherein R_a is the alkylene portion of the dicarboxylic acid and is a cyclic, linear, or branched alkylene of 2 to 36 carbon atoms, optionally including up to 1 heteroatom per 3 or 10 carbon atoms of the diacid; and

wherein R_b is a direct bond or a linear or branched alkylene group of 2 to 60 carbon atoms and R_c and R_d are individually a linear or branched alkyl group of 1 to 8 carbon atoms, or R_c and R_d connect together to form a single linear or branched alkylene group of 1 to 8 carbon atoms or optionally with one of R_c and R_d is connected to R_b at a carbon atom, more desirably R_c and R_d being an alkyl group of 1 or 2 to 4 carbon atoms.

6. A polymer composition comprising the reaction product of: (i) a polyol component comprising a telechelic polyamide; and (ii) an aliphatic polyisocyanate component; and optionally (iii) a chain extender component;

wherein the telechelic polyamide comprises:

a) two functional end groups selected from hydroxyl, carboxyl, or primary or secondary amine; and

b) a polyamide segment wherein: (i) said polyamide segment comprises at least two amide linkages characterized as being derived from reacting an amine with a carboxyl group; (ii) said polyamide segment comprises repeat units derived from polymerizing two or more monomers selected from the group consisting of lactam monomers, aminocarboxylic acids monomers, dicarboxylic acids monomers, and diamine monomers; and (iii) at least 25 mole percent of the amide linkages are derived from reacting a secondary amine group with a carboxyl group;

where said telechelic polyamide is characterized as a liquid with a viscosity of less than 100,000 cps at 70°C as measured by a Brookfield circular disc viscometer with the circular disc spinning at 5 rpm; and

wherein said telechelic polyamide is characterized by a number average molecular weight from about 200 to 10,000 g/mole and comprises a diversity of amide forming repeating units disrupting hydrogen bonding between amide components.

7. The polymer composition of any of the claims 1 to 6 wherein the reaction product further comprises one or more polyether segments, polyester segments and/or polycarbonate segments, wherein said segments are chemically bound into said reaction product or physically blended with said reaction product.

8. The polymer composition of any of the claims 1 to 7 wherein component (ii), the aliphatic polyisocyanate component, comprises isophorone diisocyanate (IPDI), 1,4-cyclohexyl diisocyanate (CHDI), hexamethylene diisocyanate (HDI), 4,4'-Methylene dicyclohexyl diisocyanate (H_{12} MDI), 1,6-diisocyanato-2,2,4,4-tetramethyl hexane (TMDI), 1,10-decane diisocyanate, trans-dicyclohexylmethane diisocyanate (HMDI),

xylylene diisocyanate (XDI), m-tetramethyl xylylene diisocyanate (TMXDI), or any combination thereof.

9. The polymer composition of any of the claims 1 to 8 wherein component (iii), the chain extender component, comprises one or more short chain glycols having from about 2 to about 20 carbon atoms.

10. The polymer composition of any of the claims 1 to 9 wherein component (iii), the chain extender component, comprises ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, triethylene glycol, cis-trans-isomers of cyclohexyl dimethylol, neopentyl glycol, 1,4-butanediol, 1,6-hexandiol, 1,3-butanediol, and 1,5-pentanediol, benzene glycol (HQEE), xylylene glycols, resorcinol, catechol, 1,3-propanediol, 1,12-dodecandiol, 1,9-nonanediol or any combinations thereof.

11. An article comprising the polymer composition of any of the claims 1 to 9.

12. The article of claim 11 wherein the article is an injection molded article, an article of automotive exterior, an electronic component, or an extruded film.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2015/041059

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G18/48 C08G18/60 C08G18/65 C08G18/24 C08G18/32
C08G18/50 C08G18/66
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2014/126743 A1 (LUBRIZOL ADVANCED MAT INC [US]) 21 August 2014 (2014-08-21) claims; examples	1-12
X	WO 2008/070762 A1 (ARIZONA CHEM [US]; LOCKO GEORGE ALLISON [US]; PAVLIN MARK STANLEY [US]) 12 June 2008 (2008-06-12) claims; examples; tables 1,2	1-12
X	US 4 452 922 A (SPERANZA GEORGE P [US] ET AL) 5 June 1984 (1984-06-05) claims; example 3	1-12

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2015	15/10/2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2015/041059

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014126743 A1	21-08-2014	TW 201439204 A	16-10-2014
		WO 2014126743 A1	21-08-2014
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