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(54) **Title:** INJECTION MOLDABLE AMIDE-IMIDE COPOLYMERS

(57) **Abstract**

Injection moldable copolymers are prepared from fully or partially acylated aromatic diamines and aromatic tricarboxylic anhydride compounds, aromatic dicarboxylic acides or mixtures of aromatic tricarboxylic acid anhydrides and aromatic dicarboxylic acids. These copolymers are useful for the preparation of injection molded articles and fibers.

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INJECTION MOLDABLE AMIDE-IMIDE COPOLYMERS

BACKGROUND OF THE INVENTION

Field of the Invention

The field of the invention relates to the preparation of random linear injection moldable amide-imide copolymers which process comprises reacting fully or partially acylated aromatic diamines with aromatic tricarboxylic acid anhydrides, arpomatic dicarboxylic acids or mixtures of aromatic tricarboxylic acid anhydrides and aromatic dicarboxylic acids and to novel polytrimellitic amide-imide copolymers and copolyamides and to molded objects and fibers prepared from these copolymers and copolyamides.

Background

Amide-imide and polyamide polymers and copolymers are a relatively new class of organic compounds known for their solubility in nitrogen containing solvents when in the polyamic acid form. The major application of these amide-imides has been as wire enamels and film formers. This is illustrated in U.S. Patents 3,852,106 (1974), 3,817,942 (1974), 3,661,832 (1972), 3,454,890 (1970) and 3,347,942 (1967). British Specification 570,858 (1945) discloses the general state of the art.

Polyimide and polyamide-imide polymers have also been found useful for molding applications as shown in U.S. Patents 4,016,140 (1977), 3,654,227 (1972) and 3,573,260 (1971).

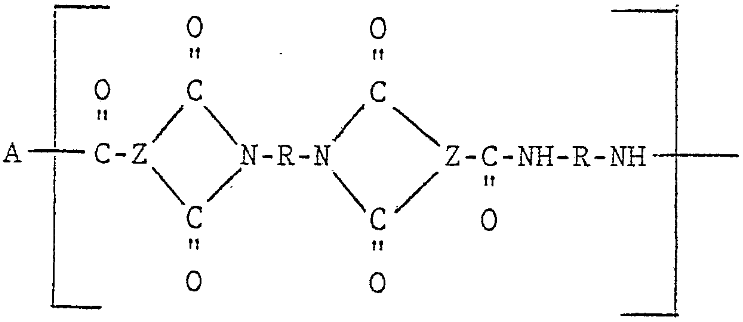
The general object of this invention is to provide injection moldable amorphous linear amide-imide copolymers and polyamides. A more specific object of this invention is to provide a novel process for the manufacture of injection moldable amide-imide and amide copolymers and copolyamides by reacting fully or partially acylated aromatic diamines with aromatic tricarboxylic acid anhydrides, aromatic dicarboxylic acids, or mixtures of aromatic dicarboxylic acids and aromatic tricarboxylic acid anhydrides. Another object is to provide novel polyamide-imide or polyamide polymers or copolymers suitable for use as an engineering plastic particularly for and in injection molding. Other objects appear hereinafter.

We have discovered a novel melt condensation process in which fully or partially acylated aromatic diamines are reacted with aromatic tricarboxylic anhydrides, aromatic dicarboxylic acids or mixtures of aromatic tricarboxylic acid anhydrides with aromatic dicarboxylic acids to yield engineering plastics suitable for injection molding which feature very high tensile strength and heat distortion temperatures. Our novel process for the preparation of random linear injection moldable amide-imide and amide copolymers and copolyamides comprises reacting fully or partially acylated aromatic diamines with aromatic tricarboxylic acid anhydrides, aromatic dicarboxylic acids or mixtures of aromatic tricarboxylic acid anhydrides with aromatic dicarboxylic acids in a molar ratio of about 9:1 to about 1:9 at a temperature of about 150 to 750°F.

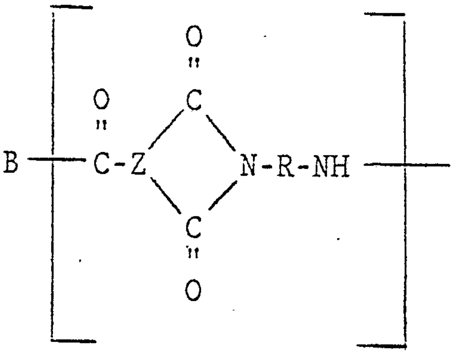
In the prior art, melt reaction of aromatic tricarboxylic acid anhydride compounds with aromatic diamines have produced products which are not suitable for injection molding application. The reason for this is not known, but it is specified that various side reactions occur. It has now been discovered that when fully or partially acylated aromatic diamines are reacted, injection molding grade polyamide-imide copolymers are produced. In our process we usually acylate more than half of the diamines utilized in the reaction. The preferred acylation is about 70 to 100 percent of the total amine functionality.

Evidence for linearity for our novel copolymer is demonstrated by the solubility of the polymer. Polymers produced from aromatic tricarboxylic acid anhydride compounds such as trimellitic acid anhydride and aromatic diamines via various melt polymerization methods generally show little or no solubility for products having inherent viscosity in excess of 0.5. The copolymer produced according to the novel process utilizing partially or fully acylated diamines is essentially soluble after curing with inherent viscosities in the range of 0.6 to 3.0. For the purpose of this invention, inherent viscosity is measured at 25°C and 0.5% w/v in 100% sulfuric acid or N-methylpyrrolidone.

The novel injection moldable amorphous random linear polyamide-imide copolymers of this invention can comprise units of:



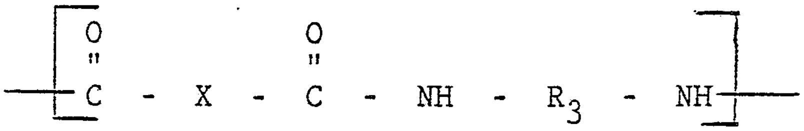
and units of:



R comprises R_1 and R_2 where R_1 and R_2 are divalent aromatic hydrocarbon radicals of from 6 to about 20 carbon atoms or two divalent hydrocarbon radicals of from 6 to 20 carbon atoms joined directly or by stable linkages selected from the group consisting of -O-,

-SO-, methylene, -CO-, $-SO_2-$, and -S- radicals and wherein said R_1 and R_2 containing units run from about 10 mole percent R_1 containing unit and about 90 mole percent R_2 containing unit to about 90 mole percent R_1 containing unit and about 10 mole percent R_2 containing unit.

The novel injection moldable random linear copolymer may comprise structural Units A and B and may also include 10% to 100% of Unit C of the following formula:



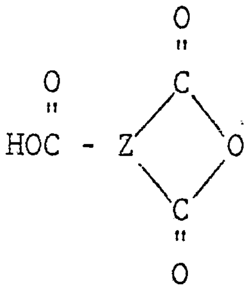
$$\left[\overset{O}{\overset{\|}{C}} - X - \overset{O}{\overset{\|}{C}} - NH - R_3 - NH \right]$$

wherein X is a divalent aromatic radical usually a divalent benzene radical and R_3 comprises both R_1 and R_2 as defined above or is equal to R_1. Furthermore, if structure C is present R of structural Units A and B, if present, can be equal to R_1 or comprise both R_1 and R_2 as set forth above.

In the foregoing structural units Z is a trivalent aromatic radical. Z may be a trivalent radical of benzene, naphthalene, biphenyl, diphenyl ether, diphenyl sulfide, diphenyl sulfone, ditolyl ether, and the like.

Useful aromatic tricarboxylic acid anhydrides which contribute the trivalent radical moiety of Z include those compounds containing at least one pair of carboxyl groups in the ortho position with respect to each other or otherwise situated in a fashion which permits the formation of an anhydride structure, one other carboxyl group and from 9 to 21 carbon atoms. Within these limits, these compounds may contain one or more benzenoid rings such as, for instance, trimellitic anhydride and its isomers and multi-ring compounds such as the 1,8-anhydride of 1,3,8-tricarboxylnaphthalene. Usually these compounds contain up to three benzenoid rings.

The aromatic tricarboxylic acid anhydride used in the novel process to form the polyamide-imide polymers of this invention is of the formula:



where Z is a trivalent aromatic radical defined as set forth hereinabove. The following aromatic tricarboxylic anhydrides are preferred: trimellitic acid anhydride; 2,3,6-naphthalene tricarboxylic anhydride; 1,5,6-naphthalene tricarboxylic anhydride, and the like; 2,6-dichloronaphthalene-4,5,7-tricarboxylic anhydride, and the like. One of the preferred aromatic tricarboxylic anhydrides is trimellitic anhydride since this compound is readily available and forms polymers having excellent physical properties of tensile strength and elongation and is resistant to high temperatures.

Suitable fully or partially acylated aromatic diamines useful in applicant's process include <u>para</u>- and <u>meta</u>-phenylenediamine, <u>para</u>- and <u>meta</u>-xylenediamine, <u>para</u>-toluenediamine, 2,4-toluenediamine, 2,6-toluenediamine, 3,5-toluenediamine, oxybis-(aniline), thiobis(aniline), sulfonylbis(aniline), diaminobenzophenone, methylenebis(aniline), benzidine, 1,5-diaminonaphthalene, oxybis(2-methylaniline), thiobis(2-methylaniline), and the like. Examples of other useful aromatic primary diamines are the following: 2,2'-naphthalene diamine, 2,4'-naphthalene diamine, 2,2'-biphenylene diamine, 3,3'-biphenylene diamine, 4,4'-biphenylene diamine, and the like; 3,3'-dichlorobenzidine, ethylene dianiline (4,4'-diaminodiphenyl ethane), and the like; ketodianiline, 3,3'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, hexafluoroisopropylidene-bis(4-phenyl amine), 4,4'-diaminodiphenyl methane, 2,6-diaminopyridine, bis-(4-aminophenyl)diethyl silane, bis(4-aminophenyl)ethyl phosphine oxide, bis(4-aminophenyl)-N-phenylamine, bis(4-aminophenyl)-N-methylamine, 3,3'-dimethyl-4,4'-diaminobiphenyl, <u>para</u>-bis(2-methyl-4-aminophenyl)benzene, 3,3'-diaminoadamantane.

Useful aromatic dicarboxylic acids include isophthalic acid and terephthalic acid. In applicant's process further preparation of injection moldable amide-imide and amide copolymers process can be conducted without utilizing a solvent or fluidizing agent though it is preferred to use agents such as N-methylpyrrolidone, dimethylacetamide, or acetic acid for the initial mixing of reactants. In general, since these polymers are linear, they may be easily cured in the melt using a twin screw extruder as the finishing reactor instead of a solid state polymerization. However, in some instances, it may be helpful to solid state polymerize the copolymers. The term "solid state polymerization" refers to chain extension of polymer molecules under conditions where the polymer particles contain their solid form and do not become a fluid mass.

The solid state polymerizing can be carried out below the melting point of the copolymer and can be conducted in several ways. However, all the techniques require heating the ground or pelletized copolymer below the copolymer melting point, generally of about 400 to 600°F while either sparging with an inert gas such as nitrogen or operating under vacuum.

Injection molding of the novel copolymer is accomplished by injecting the copolymer into a mold maintained at a temperature of about 250-500°F. In this process a 0.1-2.0 minutes cycle is used with a barrel temperature of about 500°F to 700°F. The injection molding conditions are given in Table I.

TABLE I

Mold Temperature	250-500°F
Injection Pressure	2,000-40,000 psi and held for 0.5-20 seconds
Back Pressure	0-400 psi
Cycle Time	6-120 seconds
Extruder:	
Nozzle Temperature	500°F to 700°F
Barrel Temperature	500°F to 700°F
Screw:	
10-200 revolutions/minute	

The mechanical properties of the polymers prepared in the Examples are given in Tables II, III, IV, V, VI, VII and VIII.

In applicant's process the acylated aromatic diamines need not be isolated or purified prior to their further reaction with the tricarboxylic acid anhydride compound or mixture of the tricarboxylic acid anhydride with dicarboxylic acid or with a mixture of isophthalic and terephthalic acid or just with isophthalic or terephthalic acid. Therefore, one can react one to two moles of acetic anhydride or acid or propionic anhydride or acid or any other C_2 through C_8 containing aliphatic acid or C_4 through C_{16} containing aliphatic anhydride and one mole of the appropriate aromatic diamine or diamine mixture and use the resulting acylated diamine solution in acetic acid or propionic acid to react with the aromatic tricarboxylic anhydride compound, or mixtures of the tricarboxylic anhydride compound with aromatic dicarboxylic acid, or dicarboxylic acids. It should be noted that formic anhydride or acids cannot be used to acylate the diamines in this process.

In most cases, linear high molecular weight aromatic polyamide-imide or polyamide polymers or copolymers result after melt and/or solid state polymerization. Acylating agents include acetic anhydride, acid or propionic acid or anhydride, etc., or any aliphatic acid or anhydride containing from 2 to 8 carbon atoms per acid, preferably 2 to 4 carbon atoms per acid or 4 to 16 carbon atoms per anhydride, preferably 4 to 8 carbon atoms. Formic acid cannot be used as an acylating agent in this process.

The following examples illustrate the preferred embodiments of this invention. It will be understood that these examples are for illustrative purposes only and do not purport to be wholly definitive with respect to the conditions or scope of the invention.

The novel process can suitably be conducted as a continuous process, which process comprises reacting fully or partially acylated aromatic diamines with aromatic tricarboxylic acid anhydrides, aromatic dicarboxylic acids or mixtures of aromatic dicarboxylic acids and aromatic tricarboxylic acid anhydrides in a molar ratio of about 9:1 to 1:9 at a temperature of about 150 to 750°F and wherein the molar ratio of the diamines to the anhydride or acid, or acid and anhydride mixture is 0.9:1 to 1.1:1, and wherein at least 50% of the amine functionality is acylated.

Suitably the molded polymers can also be filled from about 20 to 60 weight percent with glass fibers, glass beads, mineral fillers or mixtures thereof. The preferred polymer which can be filled is prepared from meta toluene diamine and a mixture of terephthalic and isophthalic acid. Advantageously the aforementioned molding composition may contain from about 30 to 50 weight percent of glass fiber, glass beads, mineral fillers or mixtures thereof.

EXAMPLE 1

Metaphenylenediamine (540g) and acetic acid (900 ml) were placed in a five liter three-necked round bottom flask equipped with mechanical stirrer, pressure equalizing addition funnel and nitrogen sparge tube, and distillation head and condenser. The nitrogen sparge was set at 300 cc/min. and 765g of acetic anhydride was added over 5 min. This was followed by the addition of 415g of isophthalic acid and 480g of trimellitic anhydride. The temperature of the bottom half of the spherical heating mantle surrounding the flask was set at 700°F and the top half of the mantle was heated with a Variac set at 50. After 105 min., 1730 ml of distillate was collected and the polymer had become very viscous. The heat was turned off and the polymer was cooled under nitrogen. The inherent viscosity of the polymer 0.5% w/v in 60:40 w/w phenol:tetrachloroethane at 25°C was 0.14 dl/g.

EXAMPLE 2

Oxybisaniline (OBA) (280g), metaphenylenediamine (MPDA) (64.8g), and 500 ml of N-methylpyrrolidone (NMP) were charged into a 3 liter 3-necked flask equipped with a metal-blade, metal shaft stirrer, pressure equalizing addition funnel with nitrogen inlet, and a distillation take off. After flushing the flask with nitrogen and keeping a slow bleed, acetic anhydride (204g) was added over 5 min. to this stirred mixture during which time the exothermic acylation raised the temperature to 175-200°F. Trimellitic anhydride (384g) was added quickly to this solution. After a short induction period, the TMA dissolved and reacted as evidenced by a further rise in solution temperature to 250°F. Finally 2g of trisnonylphenylphosphite was added to the solution. The temperature of the bottom half of the spherical heating mantle surrounding the flask was set to 600°F, while a Variac connected to the top half was set to 50. After 80 min. of heating, 730 ml of solvent, water, and acetic acid had distilled, during which time an extremely viscous polymer was formed. The polymer was soluble in 60:40 w/w phenol:tetrachloroethane (TCE), NMP, and 100% sulfuric acid. Its inherent viscosity (0.5% w/v in 60:40 w/w phenol:TCE) was 0.23. The polymer was cured under high vacuum overnight at 270°C to give material with an inherent viscosity of 1.36 in 100% sulfuric acid or 0.80 in NMP (0.5% w/v at 25°C). The polymer could be easily compression molded (5 min. at 700°F) to produce specimens with a tensile strength of 6,500 psi. Annealing these parts 16 hr. at 450°F and 100 hr. at 500°F produced specimens (without distortion) having a tensile strength of 14,000 psi.

EXAMPLE 3

Example #2 was repeated with the exception that 396g of methylenebisaniline was substituted for the mixture of OBA and MPDA. Polymer was produced which had an inherent viscosity of 0.23 in 60:40 w/w phenol:tetrachloroethane or 0.25 in 100% sulfuric acid. Curing the polymer 16 hr. at 270°C under high vacuum raised the inherent viscosity to 1.43 in 100% sulfuric acid. The polymer could be compression molded at 700°F to produce amber glass colored plaques.

EXAMPLE 4

Fully aromatic TMA:oxybisaniline:metaphenylene diamine (MPDA) (in a molar ratio of 1:0.7:0.3) polyamide-imide was prepared according to the procedure set forth in Example 3 and the copolymer had an inherent viscosity of 0.35. The copolymer was then solid state polymerized raising the inherent viscosity to 0.80. The resulting copolymer was then injected on the Arburg injection molding equipment using mold temperatures of 410°F to 440°F and barrel temperatures of 610°F to

640°F. Some of the molded specimens were then annealed for 48 hours at 470°F followed by 96 hours at 500°F. The physical properties of these copolymers are listed in Table II. They had tensile strength of 25,600 to 26,100 p.s.i., elongation of 9.5% and flexural strength of 32,600 to 35,600. After annealing, the copolymer is still soluble up to 90% with very little change in inherent viscosity taking place.

TABLE II

Properties of Injection Molded Fully Aromatic Amide-Imide Polymer (OBA:MPDA 70:30)

	ASTM Method	
Mold Temperature, °F		440
Annealed		No
Tensile Strength, psi	D-638	16,800
Tensile Modulus, psi	D-638	585,000
Percent Elongation	D-638	3.8
Flexural Strength, psi	D-790	23,100
Flexural Modulus, psi	D-790	682,000
Tensile Impact, ft-lb/in^2	D-1822	12.0
H.D.T. @ 264 psi, °F	D-648	480°F

TABLE II (Cont.)

	ASTM Method		
Mold Temperature, °F		410	440
Annealed		Yes	Yes
Tensile Strength, psi	D-638	26,100	25,600
Tensile Modulus, psi	D-638	524,000	519,000
Percent Elongation	D-638	9.5	9.6
Flexural Strength, psi	D-790	35,600	32,600
Flexural Modulus, psi	D-790	711,000	644,000
Tensile Impact, ft-lb/in^2	D-1822	87.7	64.6
H.D.T. @ 264 psi, °F	D-648	-	-

EXAMPLE 5

Copolymers were prepared as in Example 4, but polymers with different inherent viscosities were injected to mold an 8 1/2" long Type I tensile bar. The molding was done on a 10 ounce Stokes molding machine. These copolymers were easy to anneal and the properties before and after annealing are listed in Table III.

TABLE III

Mechanical Properties of the Injection Molded TMA:OBA:MPDA 10:7:3 Polymer from Type I Tensile Specimens

	As Molded	Annealed[a]	ASTM Method
Tensile Strength, psi	9,900	23,700	D-638
Tensile Modulus, psi	698,000	661,000	D-638
Percent Elongation	2.1	9.7	D-638
Flexural Modulus, psi	770,000	680,000	D-790
Izod, ft-lb/in notch	0.53	1.7	D-256
Shrinkage		2.5%	

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[a] 16 hr @ 480°F, 24 hr @ 490, 72 @ 500.

EXAMPLE 6

Melt preparation of TMA:OBA:MPDA 10:6:4 copolymer

Oxybisaniline (480g), metaphenylenediamine (172.8g) and acetic acid (945g) was charged into a five-liter three-necked flask equipped with a metal-blade, metal shaft stirrer, pressure equalizing addition funnel with nitrogen inlet, and a distillation takeoff. After flushing the flask with nitrogen and keeping a slow bleed, acetic anhydride (408g) was added over two minutes. This was followed by the addition of 768g of trimellitic anhydride over one minute. The temperature of the bottom half of the spherical heating mantle surrounding the flask was set at 725°F and the Variac connected to the top half was set at 50. After 86 minutes approximately 1400 ml of distillate was collected, the polymer was briefly held under low vacuum (20 in Hg) and then cooled under nitrogen. Its inherent viscosity (0.5% w/v in NMP @ 25°C) was 0.24. The polymer was cured under high vacuum (0.8 mm Hg) for 16 hr @ 535°F increasing its inherent viscosity to 0.75. The physical properties are set forth in Table IV.

TABLE IV

Mechanical Properties of the Injection Molded TMA:OBA:MPDA 10:6:4 Polymer

	As Molded	Annealed[a]	ASTM Method
Tensile Strength, psi	12,400	26,500	D-638
Percent Elongation	3.7	12.1	D-638
Flexural Strength, psi	28,100	32,500	D-790
Flexural Modulus, psi	674,000	652,000	D-790
Izod, ft-lb/in notch	1.5	3.5	D-256
H.D.T. @ 264 psi	513	532	D-648
Shrinkage,[b] %		0.7	

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[a] 16 hr @ 495, 24 hr @ 505, 24 hr @ 519.

[b] In length of D1708 tensile bar during annealing.

Samples of this copolymer were annealed under different conditions to determine the effect of annealing upon physical properties and dimensional stability of the test specimens. Results of the mechanical property tests are listed in Table V. Annealing cycles are also set forth in Table V.

TABLE V

Effect of Annealing Cycle on Properties of the Injection Molded TMA:OBA:MPDA 10:6:4 Polymer

	ASTM Method	As Molded	I
Annealing Cycle			
Tensile Strength, psi	D-638	12,400	26,500
Percent Elongation	D-638	3.7	12.1
Flexural Strength, psi	D-790	28,100	32,500
Flexural Modulus, psi	D-790	674,000	652,000
Izod, ft-lb/in notch	D-256	1.5	3.5
H.D.T. @ 264 psi	D-648	513	532
Shrinkage,[a] percent		-	0.7
Annealing Cycle		II	III
Tensile Strength, psi	D-638	26,400	26,100
Percent Elongation	D-638	15	12.0
Flexural Strength, psi	D-790	31,900	-
Flexural Modulus, psi	D-790	619,000	-
Izod, ft-lb/in notch	D-256	4.2	-
H.D.T. @ 264 psi	D-648	530	-
Shrinkage,[a] percent		0.6	0.9

I 16 hr @ 495°F, 24 @ 505, 24 @ 519.
II 30 hr @ 495, 15 @ 508, 20 @ 515, 24 @ 520.
III 24 hr @ 509, 24 @ 520.
a Of the D1708 T-bar.

EXAMPLE 7

A copolymer was prepared similar to the procedure set forth in Example 6, but having the molar ratio of TMA:OBA:MPDA of 10:4:6.

Samples of this copolymer were injection molded and then annealed under different conditions to determine the effect of annealing upon physical properties and dimensional stability of the test specimens. Results of the mechanical property tests are listed in Table VI. Annealing cycles are also set forth in Table VI.

TABLE VI

Effect of Annealing Cycle on the Properties of the Injection Molded 10:4:6 TMA:OBA:MPDA Polymer

	ASTM Method	As Molded	I
Annealing Cycle			
Tensile Strength, psi	D-638	19,400	25,700
Percent Elongation	D-638	6.9	15
Flexural Strength, psi	D-790	32,500	32,100
Flexural Modulus, psi	D-790	653,000	600,000
Izod, ft-lb/in notch	D-256	2.1	2.1
H.D.T. @ 264 psi	D-648	519	547
Shrinkage,[a] percent			0.4

TABLE VI (Cont.)

Annealing Cycle	ASTM Method	II	III
Tensile Strength, psi	D-638	25,700	24,100
Percent Elongation	D-638	15	9.8
Flexural Strength, psi	D-790	32,800	-
Flexural Modulus, psi	D-790	676,000	-
Izod, ft-lb/in notch	D-256	3.1	-
H.D.T. @ 264 psi	D-648	550	-
Shrinkage,[a] percent		0.47	0.7

I 30 hr @ 495°F, 15 @ 508, 20 @ 515, 24 @ 520.
II 24 hr @ 509, 24 @ 520.
III 24 hr @ 520.
a - Of the D1708 T-bar.

EXAMPLE 8--Preparation of TMA:OBA:MPDA 10:6:4 Copolymer Prepared From 90% Acylated Diamines

A copolymer was prepared similar to the procedure set forth in Example 6 except that 1.8 moles of acetic anhydride per mole of diamine were used such that the diamines would be 90% acylated.

The copolymer had an inherent viscosity of 0.7. The sample was injection molded and annealed. Its mechanical properties are listed in Table VII.

TABLE VII

Mechanical Properties of 10:6:4 Trimellitic Anhydride:Oxybisaniline:Metaphenylenediamine Polymer Prepared from 90% Acylated Diamines

	ASTM Method	Unannealed	Annealed[a]
Tensile Strength, psi	D-638	13,100	25,100
Percent Elongation	D-638	3.5	11.5
Flexural Strength, psi	D-790	23,900	31,600
Flexural Modulus, psi	D-790	710,000	673,000
Izod, ft-lb/in notch	D-256	1.4	3.7
Heat Distortion Temperature @ 264 psi	D-648	467°F	519°F

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[a] Annealing cycle: 16 hr @ 490°F, 24 hr @ 504°F, 24 hr @ 510°F, 24 hr @ 520°F.

EXAMPLE 9

This example illustrates the continuous melt preparation of 10:6:4 TMA:OBA:MPDA copolymer using 90% acylated diamines.

A twenty-five gallon stirred kettle was charged with 18,000g (90 mole) of oxybisaniline, 6480g (60 mole) of metaphenylenediamine, and 12 l. (12,600g) of acetic acid. To this stirred mixture under nitrogen was added 27,560g (270 mole) of acetic anhydride over a period of 12 minutes while the skin of the jacketed kettle was water cooled. During the addition, the temperature of the kettle contents increased from 91°F to 250°F. Trimellitic anhydride, 28,800g (150 mole) was added to the kettle over a period of 5 minutes during which time the temperature of the contents dropped to 190°F. This mixture was heated to 240°F by passing steam through the kettle's jacket. This mixture was continuously metered at a rate of 13,200g/hr into an electrically heated (skin temperature 640°F) helical anchor stirred reactor. The feed stream into this reactor was maintained at approximately 150 psi and the stream was heated to a temperature of 420-440°F. The reactor content was maintained at 2,500-3,000g and a melt temperature of 575-600°F. Distillate was collected at a rate of 6,300-6,400g/hr and product was pumped out of the reactor by a gear pump at a rate of 6,750-6,850g/hr into a water bath. The product polymer had an inherent viscosity of 0.29 in N-methylpyrrolidone @ 25°C and 0.5% w/v concentration.

This polymer was passed through an 8.2 ft. long Egan twin screw reactor having 3.5 in. diameter screws, operating at 26 RPM and a throughput of 66-70 lb/hr. The four zone temperatures were set at 550, 630, 670, and 640°F and melt temperature indicators in these zones showed temperatures in the range of 600-626, 672-689, 679-696, and 695-724°F. The extruder barrel was vented and vacuum was applied. The inherent viscosity of the polymer increased to 0.66 to 0.80 during this operation.

EXAMPLE 10

m-Toluenediamine (MTDA 80/20 mixture of the 2,4 and 2,6 isomers) (407g, 3.33 moles) and acetic acid (680g) were placed in a 5 liter 3-necked round bottom flask equipped with mechanical stirrer, pressure equalizing addition funnel and nitrogen sparge tube, and distillation head and condenser. The nitrogen sparge was set at 375 cc/min. and acetic anhydride (680 g, 6.67 mole) was added over 8 min. This was followed by the addition of 277g (1.67 mole) of isophthalic acid (IA) and 277g (1.67 mole) of terephthalic acid (TA). The temperature of the heating mantle surrounding the bottom half of the flask was set at 550°F. After 105 min. approximately 1200 ml of distillate had been collected and the temperature of the mantle was set at 700°F. After 35 min. more an additional 140 ml of distillate was collected. The melt was then stirred for 20 min. under low vacuum (150 torr), cooled with liquid nitrogen, and ground. The inherent viscosity of the polymer 0.5% w/v in N-methylpyrrolidone at 25°C was 0.15. Solid state polymerizations for 16 hours at 460°F, 16 hours at 465°F and 16 hours at 490°F under high vacuum (0.25 torr) increased the inherent viscosity to 0.31, 0.43 and 0.81 after each successive solid state polymerization. The polymer was injection molded and annealed. Its mechanical properties are listed in Table VIII.

TABLE VIII

Properties of the Fully Aromatic 1:1:2 TA:IA:MTDA Polyamide

	As Molded	Annealed[a]	Annealed[b]
Tensile Strength, psi	14,000	16,000	17,200
Elongation at Break, %	4.1	4.5	5.0
Flexural Strength, psi	28,900	32,200	--
Flexural Modulus, psi	643,000	646,000	--
Izod ft-lb/in notch	0.13	0.14	--
Tensile Impact ft-lb/in^2	31.9	34.2	41.6
H.D.T. @ 264 psi, °F	445	510	--

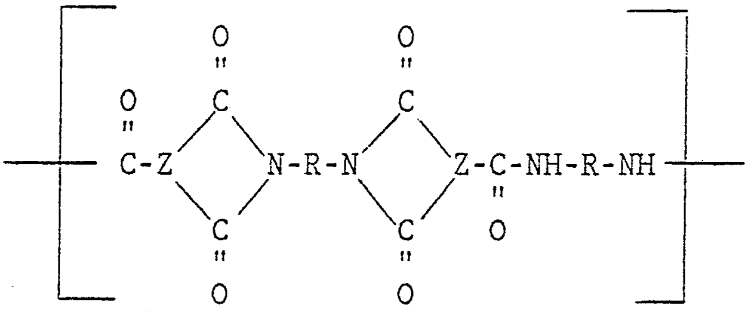
[a] Annealing Cycle 24 hr. @ 490°F, 24 hr. @ 500°F.
[b] Annealing Cycle 24 hr. @ 490°F, 96 hr. @ 500°F.

EXAMPLE 11

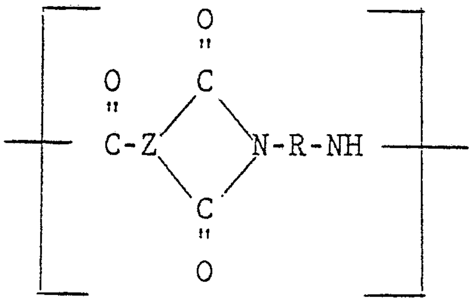
Polymer prepared according to Example 10, which had an inherent viscosity of 0.52, was blended with 30% by weight of fiber glass. The mixture was injection molded and displayed excellent mechanical properties.

We claim:

1. A process for the preparation of random linear injection moldable amide-imide and amide copolymers which process comprises reacting fully or partially acylated aromatic diamines with aromatic tricarboxylic acid anhydrides, aromatic dicarboxylic acids or mixtures of aromatic dicarboxylic acids and aromatic tricarboxylic acid anhydrides in a molar ratio of about 9:1 to about 1:9 at a temperature of about 150 to 750°F, and wherein the molar ratio of the diamines to the anhydride or acid, or acid and anhydride mixture is about 0.9:1 to 1.1:1 and at least 50% of the amine functionality is acylated.
2. The process of Claim 1 wherein the acid is isophthalic acid.
3. The process of Claim 1 wherein the tricarboxylic acid anhydride compound is trimellitic anhydride.
4. The process of Claim 1 wherein about 70 to 100 percent of the aromatic diamine is acylated.
5. The process of Claim 4 wherein aromatic diamines contain one benzene ring or two benzene rings joined directly or by stable linkages consisting of -S-, -O-, $-\overset{O}{\overset{\|}{S}}-$, $-SO_2-$, -C- or methylene radicals.
6. The process of Claim 4 wherein the acylated diamines are prepared from oxybisaniline and metaphenylene diamine.
7. The process of Claim 6 wherein the molar ratio of the oxybisaniline to the metaphenylene diamine is in the range of about 8:2 to about 2:8.
8. An injection moldable random linear polyamide-imide copolymer prepared according to the process of Claim 1 and comprising units of:

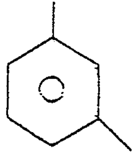


and units of:

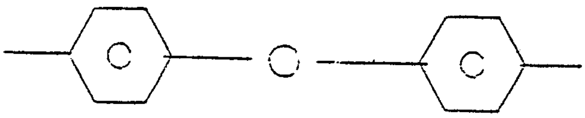


wherein "Z" is a trivalent benzene ring or lower alkyl substituted trivalent benzene ring; R comprises R_1 and R_2, R_1 and R_2 are divalent aromatic hydrocarbon radicals of from 6 to about 20 carbon atoms or two divalent hydrocarbon radicals of from 6 to 20 carbon atoms joined directly or by stable linkages selected from the group consisting of -O-, methylene, -CO-, $-SO_2-$, and -S- radicals and wherein said R_1 and R_2 containing units run from about 10 mole percent R_1 containing unit and about 90 mole percent R_2 containing unit to about 90 mole percent R_1 containing unit and about 10 mole percent R_2 containing unit.

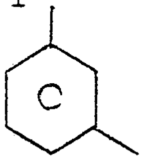
9. The copolymer of Claim 8 wherein R_1 is



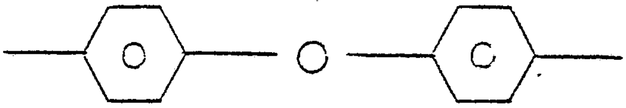
and R_2 is



10. The copolymer of Claim 8 wherein Z is a trivalent benzene ring, R_1 is



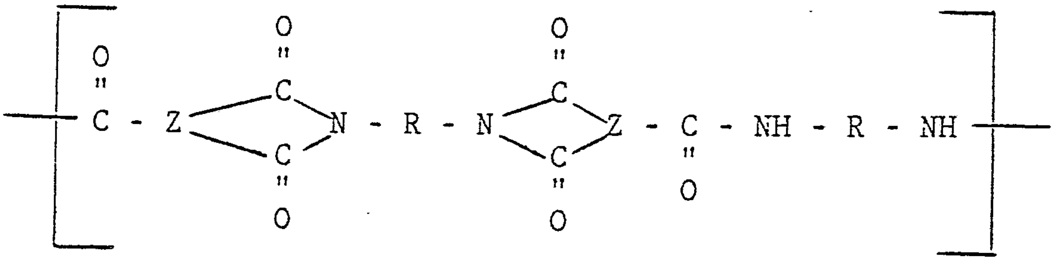
R_2 is



and wherein the concentration range runs from about 20 mole percent of the R_1 containing units and about 80 mole percent of the R_2 containing units to about 80 mole percent of the R_1 containing units and about 20 mole percent of the R_2 containing units.

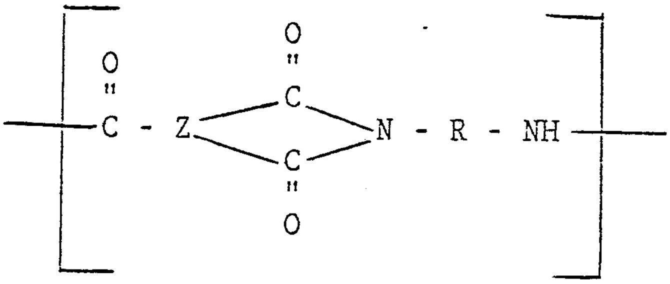
11. The copolymer of Claim 10 wherein the concentration range runs from about 40 mole percent of the R_1 containing units and about 60 mole percent of the R_2 containing units to about 60 mole percent of the R_1 containing units and about 40 mole percent of the R_2 containing units.

12. An injection moldable random linear polyamide-imide copolymer prepared according to the process of Claim 1 comprising units of



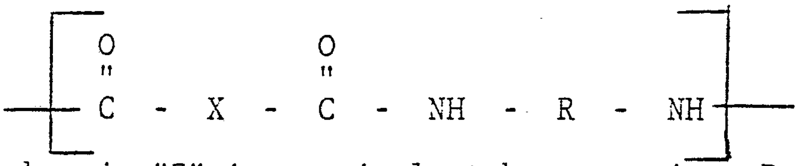
$$\left[-\overset{\overset{O}{\|}}{C}-Z\begin{array}{c}\overset{\overset{O}{\|}}{C}\\ \\ \underset{\underset{O}{\|}}{C}\end{array}N-R-N\begin{array}{c}\overset{\overset{O}{\|}}{C}\\ \\ \underset{\underset{O}{\|}}{C}\end{array}Z-\underset{\underset{O}{\|}}{C}-NH-R-NH-\right]$$

and units of



$$\left[-\overset{\overset{O}{\|}}{C}-Z\begin{array}{c}\overset{\overset{O}{\|}}{C}\\ \\ \underset{\underset{O}{\|}}{C}\end{array}N-R-NH-\right]$$

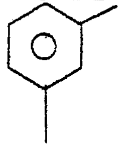
and units of



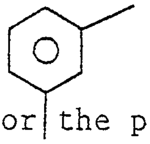
$$-\!\!\left[\overset{O}{\overset{\|}{C}} - X - \overset{O}{\overset{\|}{C}} - NH - R - NH \right]\!\!-$$

wherein "Z" is a trivalent benzene ring; R comprises R_1 or a mixture of R_1 and R_2, R_1 and R_2 are divalent aromatic hydrocarbon radicals of from 6 to about 20 carbon atoms or two divalent hydrocarbon radicals of from 6 to 20 carbon atoms joined directly or by stable linkages selected from the group consisting of -O-, methylene, -CO-, $-SO_2-$ and -S- radicals, and said R_1 and R_2 containing units run from about 10 mole percent R_1 containing units and 90 mole percent R_2 containing units to about 90 mole percent R_1 containing units to about 10 mole percent R_2 containing units and X is a divalent aromatic radical.

13. The copolymer of Claim 12 wherein X is



and R_1 is



14. A continuous process for the preparation of random linear injection moldable amide-imide and amide copolymers which continuous process comprises reacting fully or partially acylated aromatic diamines with aromatic tricarboxylic acid anhydrides, aromatic dicarboxylic acids, or mixtures of aromatic dicarboxylic acids and aromatic tricarboxylic acid anhydrides in a molar ratio of about 9:1 to 1:9 at a temperature of about 150 to 750°F and wherein the molar ratio of the diamines to the anhydride or acid, or acid and anhydride mixture is 0.9:1 to 1.1:1 and at least 50% of the total amine functionality is acylated.

15. The process of Claim 14 wherein the aromatic dicarboxylic acid is isophthalic acid.

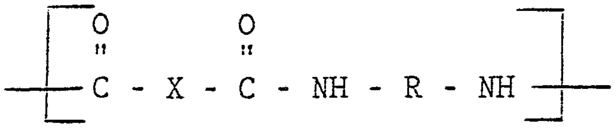
16. The process of Claim 14 wherein the tricarboxylic acid anhydride compound is trimellitic anhydride.

17. The process of Claim 14 wherein about 70 to 100 percent of the aromatic diamine is acylated.

18. The process of Claim 14 wherein the acylated diamines are prepared from oxybisaniline and metaphenylene diamine.

19. The process of Claim 18 wherein the molar ratio of the oxybisaniline to the metaphenylene diamine is in the range of about 8:2 to about 2:8.

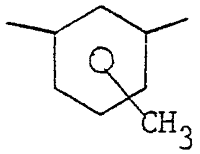
20. An injection moldable random linear polyamide copolymer prepared according to the process of Claim 1 and comprising units of



$$-\!\!\left[\overset{O}{\overset{\|}{C}} - X - \overset{O}{\overset{\|}{C}} - NH - R - NH\right]\!\!-$$

wherein R comprises R_1 or a mixture of R_1 and R_2, R_1 and R_2 are divalent aromatic hydrocarbon radicals of from 6 to about 20 carbon atoms or two divalent hydrocarbon radicals of from 6 to 20 carbon atoms joined directly or by stable linkages selected from the group consisting of -O-, methylene, -CO-, $-SO_2-$and -S- radicals, and said R_1 and R_2 containing units run from about 10 mole percent R_1 containing units and 90 mole percent R_2 containing units to about 10 mole percent R_2 containing units and X is a divalent aromatic radical.

21. The process of Claim 20 wherein R comprises



22. The process of Claim 21 wherein X is a mixture of terephthalic and isophthalic acids.

23. The process of Claim 22 wherein the molar ratio of terephthalic and isophathalic acids is in the range of 6:4 to about 4:6.

24. The copolymer produced according to Claim 1 wherein the copolymer is in the form of a molded object.

25. The copolymer produced according to Claim 11 wherein the copolymer is in the form of a molded object.

26. The copolymer produced according to Claim 12 wherein the copolymer is in the form of a molded object.

27. The copolymer produced according to Claim 14 wherein the copolymer is in the form of a molded object.

28. The copolymer produced according to Claim 19 wherein the copolymer is in the form of a molded object.

29. The copolymer produced according to Claim 20 wherein the copolymer is in the form of a molded object.

30. The copolymer produced according to Claim 23 wherein the copolymer is in the form of a molded object.

31. The composition of Claim 30 wherein the molded object contains from about 20 to 60 weight percent of glass fibers, glass beads, mineral fillers or a mixture thereof.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 81/0073

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[3]

According to International Patent Classification (IPC) or to both National Classification and IPC IPC C08G 69/04,69/26. 73/14. US CLASS 528/125,128,172,173,226,229,185,188,189,335,337,348,350,352,353. 260/37N.

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
US	528-125,128,172,173,185,188,189,226,229,335,337,348,350,352,353; 260-37N.

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US,A, 3,842,026 PUBLISHED 15 OCTOBER 1974 DIXON ET AL.	1-31
X	UK,A, 570,858 PUBLISHED 25 JULY 1945, DUPONT.	1-31
A	US,A, 2,421,024 PUBLISHED 27 MAY 1947, FROSH. FROSCH.	
A	US,A, 3,654,227 PUBLISHED 04 APRIL 1972 DINE-HART.	
A	US,A, 3,661,863 PUBLISHED 09 MAY 1972 CAMPBELL.	
A	US,A, 3,862,092 PUBLISHED 21 JANUARY 1975 FLOWERS ET AL.	
A	US,A, 3,817,942 PUBLISHED 18 JUNE 1974 KOVACS ET AL.	
A	US,A, 4,066,631, PUBLISHED 3 JANUARY 1977, DIMMIG.	

* Special categories of cited documents: [15]

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 07 MAY 1981	Date of Mailing of this International Search Report [2] 19 MAY 1981
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] Howard E. Schain HOWARD E. SCHAIN