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(21) International Application Number: PCT/US90/03030 (22) International Filing Date: 31 May 1990 (31.05.90) (30) Priority data: 388,182 31 July 1989 (31.07.89) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (72) Inventors: AKKAPEDDI, Murali, Krishna ; 40 Whitewood Drive, Morris Plains, NJ 07950 (US). GLANS, Jeffrey, Harper ; 19 Watchung Trail, Somerville, NJ 08876 (US).		(74) Agent: ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i>	
(54) Title: COPOLYMER OF DODECANE TEREPHTHALAMIDE			
$\begin{array}{c} \text{H} \qquad \qquad \text{H} \\ \qquad \qquad \\ -\text{N}[\text{CH}_2]_n \text{N}- \quad (\text{I}) \end{array}$			
(57) Abstract The present invention is an improved polyamide copolymer having monomer units including repeat units of formula (I), where n is from 10 to 14 and preferably is 12 (1,12-dodecanediamine), units derived from a symmetrical diacid or derivative of said diacid, preferably a symmetrical aromatic dicarboxylic acid. The copolymer has minor amounts, preferably 3 to 30 and more preferably 5 to 10 mol percent, of units derived from an additional comonomer.			

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COPOLYMER OF DODECANE TEREPHTHALAMIDEBACKGROUND OF THE INVENTION

5

The present invention is in the field of poly-amides, more particularly, the present invention relates to copolymers derived from long chain diamines, a sym-
10 metrical diacid or derivative thereof, and at least one specifically selected additional comonomer.

Conventional aliphatic nylons such as polycapro-
15 lactam (nylon 6), poly(hexamethylene adipamide) (nylon 6,6) have high melting points and are thermoplastically processable. However, they have undesirably high water
20 absorption characteristics, absorbing from 8 to 12 wt. percent water. Water absorption causes dimensional growth, and plasticization with a significant reduction in stiffness. This makes them unsuitable for various end use
25 applications.

Long chain aliphatic polyamides such as poly-laurolactam (nylon 12), and poly(1,12-dodecamethylene
30 dodecanamide) (nylon 12,12) have low moisture-absorbing properties, but have undesirably low melting points (below 180°C). Symmetrical rigid, aromatic diacids, such as terephthalic acid monomers used with aliphatic diamines
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-2-

having from 6 to 12 carbon atoms result in polyamides
5 having low moisture absorbing characteristics but undesir-
ably high melting points (greater than 300°C). Such
melting points are often above the nylon degradation temp-
eratures so that the polyamide cannot be melt-polymerized
10 or melt-processed.

SUMMARY OF THE INVENTION

15 The present invention is an improved polyamide
copolymer derived from a long chain diamine, preferably
RHN[CH₂]_nNHR, where n is from 10 to 14, and preferably is
20 12 (i.e., 1,12-dodecanediamine) and R is preferably H or
an alkyl carbonyl group such as CH₃C(=O)-; resulting in the
monomer repeat unit $\text{-N}(\text{CH}_2)_n\text{N-}$, and a symmetrical diacid
or derivative thereof, preferably R'C(=O)-Ar-C(=O)-R' where Ar is
25 an aromatic group, and R' is preferably -OH, alkoxy group
such as -OCH₃, or a halogen, resulting in the monomer
repeat unit -C(=O)-Ar-C(=O)- . Preferably the diacid is a sym-
metrical aromatic dicarboxylic acid. The symmetrical
30 aromatic diacid or derivative thereof is preferably
selected from the group consisting of terephthalic acid,
2,6-naphthalene dicarboxylic acid, 4,4'-biphenyl
dicarboxylic acid and dimethyl terephthalate. The
35 copolymer has minor amounts, preferably 3 to 30 and more
preferably 5 to 10 mol percent, of an additional
comonomer.

-3-

Useful and preferred additional comonomers include units derived from monomers which are difunctional. The functional groups are groups which are reactive with the amine groups of the diamine or the acid groups of the diacid. Preferred functional groups include amine groups, hydroxyl groups and carboxylic acid groups. Specific and preferred comonomers include lactams having up to 9 methylene groups, nonsymmetrical aromatic diacids, and hydroxy terminated polyolefins or polyethers. Depending upon the comonomer, the resulting polyamide copolymer will have high crystallinity and low moisture absorption, or the additional comonomer will contribute a "soft segment" making the polyamide copolymer more flexible.

Additional comonomers which result in the improved crystallinity and low moisture absorption of the polyamide copolymer are preferably present in an amount sufficient to reduce the melting point while at the same time enable the polymer to have high crystallinity and low moisture absorption properties. Preferably, the additional comonomer results in a polyamide copolymer having relatively high crystalline melting points of preferably from 250°C to 300°C, and more preferably 270°C to 290°C, high crystallinity, preferably at least 20 percent, and low moisture absorption, preferably below 5 percent, and

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-4-

more preferably below 3 weight percent based on the weight of polyamide copolymer and moisture. The additional comonomer can be preferably present in random or block segments thereby resulting in a random or block copolymer. The major blocks of polyamide are derived from the long chain diamine and the symmetrical diacid. Preferred additional comonomers include diamines and nonsymmetrical diacids. Preferred diamines include 4,9-dioxa-dodecane-1,12-diamine; 4,11-dioxa-tetradecane-1,14-diamine; caprolactam; and laurolactam. Preferred nonsymmetrical diacids include phthalic acid and isophthalic acid.

Comonomers which result in a polyamide copolymer having a flexible (low glass transition temperature, T_g), hydrophobic structure include block segments of polyolefin polyether and polysiloxane and the like. Preferred segments include telechelic amine terminated polyolefins including polyethylene, poly(ethylene-propylene), polyisobutylene, poly(ethylene-butene), and the like. Preferred polyether, is bisamino alkyl, polytetramethyleneoxide (derived from polytetrahydrofuran), and preferred polysiloxane is poly(dimethyl siloxane); i.e., alpha,-omega-bisaminoalkyl poly(dimethyl siloxane). These comonomers have been found to act as a "soft segment" when used in the form of a block copolymer. The resulting copolymer has a combination of properties including high

-5-

ductility (tensile-elongation), heat and chemical
 5 resistance, and low moisture absorption properties. They
 are useful for extrusion and molding applications.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

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The present invention is a polyamide copolymer comprising units derived from a long chain diamine preferably $\text{RHN}[\text{CH}_2]_n\text{NHR}$, where n is from 10 to 14 and
 15 preferably is 12 (i.e., 1,12-dodecanediamine); and R is preferably H or an alkyl carbonyl group such as $\text{CH}_3\overset{\text{O}}{\overset{\parallel}{\text{C}}}-$, resulting in the monomer repeat unit $-\overset{\text{H}}{\text{N}}[\text{CH}_2]_n\overset{\text{H}}{\text{N}}-$; a symmetrical diacid and derivatives thereof, preferably a
 20 symmetrical aromatic diacid and derivatives thereof, preferably $\text{R}'\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{Ar}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{R}'$, where Ar is an aromatic group, and R' is preferably $-\text{OH}$, alkoxy group such as $-\text{OCH}_3$, or a halogen resulting in the monomer repeat unit $-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{Ar}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-$;
 25 and an additional comonomer. Useful Ar 's include

 , and the like. The aromatic groups can contain substituents which do not adversely
 30 affect the properties of the polyamide copolymer. The symmetrical aromatic diacid is preferably selected from the group consisting of terephthalic acid, 2,6-naphthalene dicarboxylic acid, 4,4'-biphenyl dicarboxylic acid and
 35 dimethyl terephthalate. The preferred polyamide copolymer has units derived from 1,12-dodecanediamine copolymerized

-6-

with a terephthalic acid and the additional comonomer.
The copolymer comprises from 35 to 48.5 mol, and preferably 40 to 45 mol percent of units derived from the long chain diamine preferably dodecanediamine, from 35 to 48.5, and preferably from 40 to 45 mol percent of units derived from terephthalic acid or derivatives thereof. Additionally, the copolymer comprises at least 3, and preferably from 3 to 30, and more preferably from 5 to 10 mol percent of units derived from the additional comonomer.

A preferred embodiment has units derived from at least one additional comonomer which results in a copolymer having a relatively high melting point, high crystallinity, and has low moisture absorption characteristics. The preferred polyamide copolymer has a melting point below a copolymer derived from a corresponding long chain diamine and symmetrical diacid or derivative thereof (i.e., dodecanediamine and terephthalic acid) of the same molecular weight. The melting point of the preferred polyamide copolymer is preferably in the range of from 250°C to 300°C, and more preferably 270°C to 290°C. The polyamide copolymer is highly crystalline as measured by X-ray diffraction. The polyamide copolymer is preferably at least 20 percent, and more preferably at least 30 percent. The upper range of crystallinity is typically 40 percent mol and preferably 50 percent

-7-

crystalline. Additionally, the polyamide copolymer has low moisture absorption characteristics as measured according to ASTM D 570-81. Preferably the polyamide
5 copolymer absorbs less than 5 percent by weight, and preferably less than 3 percent by weight of moisture based on the weight of the polyamide copolymer and moisture.

10 Preferred additional comonomers which lead to co-crystallizable segments, or at least do not significantly reduce crystallinity are diamines such as 4,9-dioxa-1,12-diaminododecane; 4, 11-dioxa-tetradecane-1,14-diamine;
15 non-symmetrical diacids including isophthalic acid; lactams having up to 8 methylene groups, preferably laurolactam and caprolactam. Copolyamides made using these additional comonomers have been found to have
20 crystalline melting points of from 270-285°C, a low water absorption character of 1.7-3 percent by weight when measured according to ASTM D 570-81, good melt
25 processability, at or below 300°C, and satisfactory mechanical properties including strength and toughness. The copolyamides have been found to have excellent chemical resistance, particularly to aqueous zinc chloride
30 solutions.

Additionally, the polyamide copolymers have been found to be dimensionally stable when exposed to heat and
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-8-

moisture, and have chemical resistance to gasoline and alcohol as well as a variety of other organic materials. This makes the copolymers of the present invention useful for a variety of high-performance engineering resin applications, such as automotive under-the-hood parts, fuel lines, and fuel component parts.

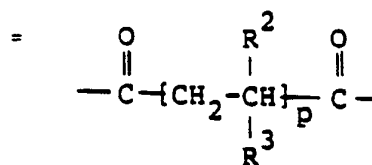
10 An alternate embodiment of the polyamide copolymer can include comonomer units to improve flexibility of the copolymer. Comonomers having a flexible hydrophobic structure resulting in a soft segment include the olefins
15 present as polyolefin segments such as polyethylene, poly(ethylene-propylene), polyisobutylene, poly(ethylene-butene), and the like. A preferred ether is a polyether such as bis[aminopropyl]polytetrahydrofuran (derived from
20 polytetramethyleneoxide); alpha,omega-bis(aminoalkyl)-poly(tetramethyleneoxide); alpha,omega-diamino polyolefins; i.e., telechelic, amino terminated
25 polyethylene; and polysiloxanes such as poly(dimethyl siloxane); i.e., alpha,omega-bisaminoalkyl poly(dimethyl siloxane). The molecular weight of the soft segments preferably range from 200 to 6,000 and more preferably from
30 750 to 2100. Polyethylene oxide is not preferred because of the high water absorption.

The additional comonomer preferably is derived

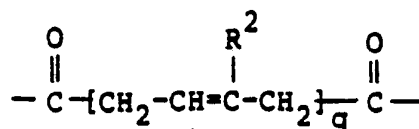
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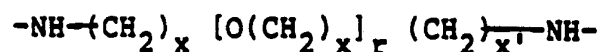
from comonomers resulting in units having the formula



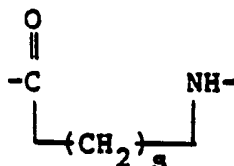
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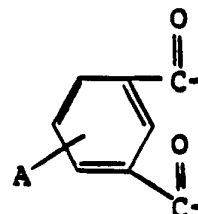
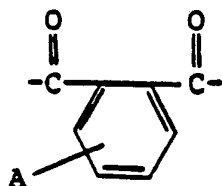
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15



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wherein

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R^2 is selected from $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{Cl}$, $-\text{CH}=\text{CH}_2$, and mixtures thereof,

R^3 is selected from $-\text{H}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{CH}-\text{CH}_2$, and mixtures thereof,

30

A is selected from H , a halogen, and a hydrocarbon having from 1 to 4 carbon atoms,

p is from 5 to 80,

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q is from 10 to 80,

-10-

r is from 1 to 30, preferably 5 to 30,

s is from 4 to 9,

x is from 4 to 6, and

5 x' is from 2 to 6.

The copolymer of the present invention can be made by conventional methods to copolymerize polyamides. Particularly preferred are melt polymerization techniques in which the monomers are melted together under an inert atmosphere. The melt polymerization preferably is conducted at from 275-320°C, and more preferably from 15 295-320°C.

In addition to the three principle monomeric constituents, which together produce the copolymer of this invention, other polymerizable monomers can also be used to prepare copolymers. Included in these are vinyl compounds and other monomers which could be polymerized directly into a linear polymer chain. The quantity of such additional monomers can vary and can be up to 30 mol percent of the total number of polymerizable constituents but preferably is limited to quantities of less than 15 30 mol percent, more preferably less than 5 mol percent.

Several Examples are set forth below to illustrate the nature of the invention and the manner of carry- 35

-11-

ing it out. However, the invention should not be considered as being limited to the details thereof. All parts are by weight unless otherwise indicated.

5

EXAMPLES

The following are Examples of copolymerizations
10 of 1,2-dodecanediamine, terephthalic acid and the indicated additional comonomer. The copolymerizations were performed in the indicated equipment with mechanical
15 stirring under a sweep of an inert gas (either nitrogen or argon). In each case the polymerizations were run until a significant increase in viscosity was noted and then the sample was allowed to cool. The resulting solid was
20 broken up and ground in a Wiley® mill to produce a powder. Melting points were determined by a differential scanning calorimetry (DSC) on a Perkin-Elmer DSC 2 calorimeter. Reduced viscosities were determined by samples dissolved
25 in m-cresol or concentrated sulfuric acid.

Samples to be tested in accordance with ASTM tests were injection molded using an Arburg® injection
30 molding machine at 320°C and 450 psi conditions. Tensile tests were performed on molded samples according to ASTM D-638 procedures.

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-12-

Water absorption measurements were performed on thin compression-molded films according to ASTM-D-570-81. Films were compression-molded at 300°C for 1 minute at 10 to 20 tons of pressure. The films were 0.1 mm thick. The films were submerged in water and their change in weight monitored until equilibrium.

10 Zinc chloride resistance was measured by immersing a bent 1/8 inch test bar in a 50 wt. percent solution of zinc chloride. The test bars were molded as described above, 7 inches long by 3/4 inch at the tabs, 1/4 inch in
15 the neck region and 1/8 inch thick (ASTM-D-638 test bars). The bars were bent 180 degrees. The appearance of the bar and its structural integrity were noted with time.

20

Comparative Example 1

A 0.5 L stainless steel resin kettle (wide mouth
25 kettle) was charged with 24.4 g (122 mmol) of 1,12-dodecanediamine, 20.3 g (122 mmol) of terephthalic acid, and 40 ml of water. The reaction mixture was slowly heated to 300°C. The material was intractable and never melted out
30 properly.

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-13-

Example 1

A 500 ml stainless steel resin kettle with a
5 mechanical stirrer was charged with 51.1 g (0.255 mol) of
1,12-dodecanediamine, 5.79 g (0.28 mol) of 4,9-dioxa-
dodecane-1,12-diamine, 44.9 (0.270 mol) of terephthalic
acid, and 50 ml of water. The polymerization mixture was
10 slowly heated to 320°C to give a clear viscous melt. The
polymer was allowed to cool and broken up. The resulting
resin was dried overnight at 110°C under vacuum.

15

Example 2

A three liter glass resin kettle was charged with
20 540.9 (2.70 mol) of 1,12-dodecanediamine, 61.3 g (0.30
mol) of 4,9-dioxadodecane-1,12-diamine, 473.5 g (2.85 mol)
of terephthalic acid and 400 ml of water. The mixture was
slowly heated 300°C. The resulting viscous melt was
25 cooled to room temperature, broken up, and dried at 100°C
under vacuum overnight.

Example 3

30

A three liter glass resin kettle was charged with
517.1 g (2.58 mol) of 1,12-dodecanediamine, 226.9 g (0.30
mol) of bisaminopropoxypolytetrahydrofuran 750, 456.0 g
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-14-

(2.74 mol) of terephthalic acid, and 400 ml of water. The mixture was slowly heated to 293°C to give a viscous melt. The melt was allowed to cool to room temperature, ground up, and dried overnight at 100°C under vacuum. This sample was unaffected by immersion in a zinc chloride solution for over one month.

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Example 4

A three liter stainless steel resin flask was charged with 336 g (1.68 mol) of 1,12-dodecanediamine, 84 g (0.112 mol) of bisaminopropoxypolytetrahydrofuran 750, 282.8 g (1.70 mol), and 250 ml of water. The mixture was slowly heated to 300°C to give a viscous melt. The reaction mass was allowed to cool to room temperature, ground up, and dried overnight at 100°C vacuum.

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Example 5

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A one liter stainless steel resin kettle fitted with a mechanical stirrer and an argon sweep was charged with 286.1 g (1.43 mol) of 1,12-dodecanediamine, 203.6 g (1.23 mol) of terephthalic acid, 22.6 g (0.14 mol) of isophthalic acid, and 400 ml of water. The kettle was slowly heated to 300°C under a sweep of argon. The resulting polymer was broken up, and dried (110°C, vacuum) overnight.

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-15-

Example 6

5 A 0.5 L stainless steel kettle was charged with
6.8 g (60.0 mmol) of caprolactam, 113.6 g (567 mmol) of
1,12-dodecanediamine, 89.7 g (540 mmol) of terephthalic
acid and 200 ml of water. The reaction mixture was slowly
10 heated to 300°C which resulted in a viscous melt. The
resulting material was allowed to cool, broken up, and
dried overnight at 110°C under vacuum.

15 Samples were tested for physical properties and
results are summarized in Table 1 below. R.V. is relative
viscosity, T_m is crystalline melt temperature.

20

Table 1

Ex.	R.V.	T _m °C	Modulus kpsi	Strength kpsi	Elongation %	Water Absorption %
25 1	1.61(*)	274,283	371	7.9	2.3	3.3
2	0.36	280,293	303	9.8	27.0	-
3	0.31	274,288	257	7.9	150.0	3.5
30 4	0.49	284,293	276	10.6	117.0	-
5	1.48(*)	284 -	367	12.0	11.3	1.7
6	-	289 -	-	-	-	2.0

* measured in m-cresol

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-16-

While exemplary embodiments of the invention have
been described, the true scope of the invention is to be
5 determined by the following claims.

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- 17 -

CLAIMS:

1. A polyamide copolymer comprising monomer repeat

units derived from the formula $\begin{matrix} \text{H} & \text{H} \\ | & | \\ -\text{N}[\text{CH}_2]_n\text{N}- \end{matrix}$ where n is from 10 to 14, units derived from a symmetrical diacid or derivative

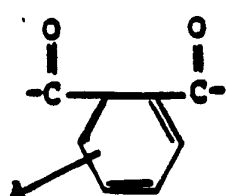
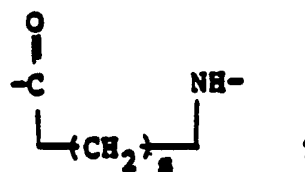
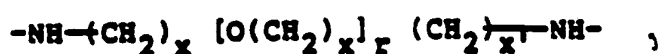
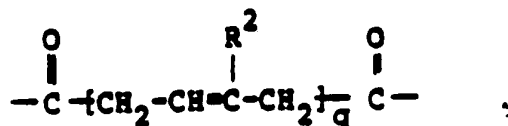
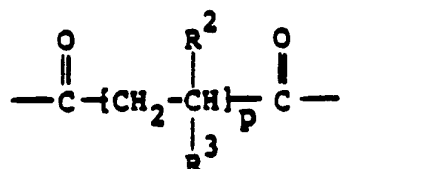
of said diacid, the repeat unit having the formula



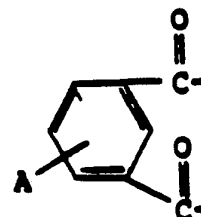
where Ar is an aromatic group,

characterized by;

further including at least one additional comonomer in monomer units having the formula



, or



- 18 -

wherein

R^2 is selected from -H, -CH₃, -C₂H₅,
-Cl, -CH=CH₂, and mixtures thereof,

R^3 is selected from -H, -CH₃, -C₂H₅,
5 -CH=CH₂, and mixtures thereof,

A is selected from H, a halogen, and a
hydrocarbon having from 1 to 4 carbon atoms,

p is from 5 to 80,

q is from 10 to 80,

10 r is from 1 to 30,

s is from 4 to 9,

x is from 4 to 6, and

x' is from 2 to 6.

15 2. The polyamide copolymer according to claim 1
further

characterized by;

the additional comonomer is derived from one or more
units selected from:

20 4,11-dioxa-tetra-decane-1,14-diamine,

4,9-dioxa-1,12diaminododecane, phthalic acid,

isophthalic acid, lactams having up to 9 methylene
groups, telechelic terminated polyolefins including
polyethylene, poly(ethylenepropylene) and

25 polyisobutylene, and telechelic amine terminated
polyolefins including bis(aminoalkyl)polytetramethylene
oxide and bis(aminoalkyl)poly(dimethylsiloxane).

30 3. The polyamide copolymer according to claim 1
or 2 further

characterized by;

sufficient units of the additional comonomer whereby
the polyamide copolymer has a melting point below a
copolymer of the same diamine and a diacid without the
35 additional comonomer and having the same molecular
weight.

- 19 -

4. The copolymer of claim 3 further
c h a r a c t e r i z e d by;
in that the diamine is 1,12-dodecanediamine.

5 5. The copolymer of claim 3 further
c h a r a c t e r i z e d by;
in that the diacid is one or more acids selected from:
terphthalic acid, derivatives of terephthalic acid,
2,6-naphthalene dicarboxylic acid, 4,4'-biphenyl
10 dicarboxylic acid, dimethyl terephthalate.

6. The copolymer according to any preceeding
claim further
c h a r a c t e r i z e d by;
15 having crystalline melting point between 250 and 300
degrees C.

7. The copolymer according to any preceeding
claim further
20 c h a r a c t e r i z e d by;
having a crystallization of at least 20 percent when
measured according by X-ray diffraction.

8. The copolymer according to any preceeding
25 claim further
c h a r a c t e r i z e d by;
having less than 5 percent by weight water absorption
when measured according to the testing standards of
ASTM D 570-81

30
9. The copolymer according to any proceeding
claim further
c h a r a c t e r i z e d by;
in consisting of up to 30 mole percent of the
35 additional comonomer.

INTERNATIONAL SEARCH REPORT

PCT/US 90/03030

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 G 69/26, C 08 G 69/36																	
II. FIELDS SEARCHED Minimum Documentation Searched ⁷ <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Classification System </td> <td style="width: 50%; border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="border-bottom: 1px solid black;">IPC⁵ </td> <td style="border-bottom: 1px solid black;">C 08 G</td> </tr> </table> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸			Classification System	Classification Symbols	IPC ⁵	C 08 G											
Classification System	Classification Symbols																
IPC ⁵	C 08 G																
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black;">Category ⁹</th> <th style="width: 70%; border-bottom: 1px solid black;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border-bottom: 1px solid black;">Relevant to Claim No. ¹³</th> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>FR, A, 2116379 (STANDARD OIL) 13 July 1972 see claims --</td> <td style="text-align: center; vertical-align: top;">1-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3790423 (F.B. JONES) 5 February 1974 see claims --</td> <td style="text-align: center; vertical-align: top;">1-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>US, A, 3843611 (R.W. CAMPBELL) 22 October 1974 see claims --</td> <td style="text-align: center; vertical-align: top;">1-9</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td>Chemical Abstract, volume 78, no. 8, 26 February 1973, (Columbus, Ohio, US), see page 64, abstract 44934x, & JP, A, 7229451 (TORAY INDUSTRIES, INC.) 2 August 1972 ----</td> <td style="text-align: center; vertical-align: top;">1-9</td> </tr> </table>			Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	FR, A, 2116379 (STANDARD OIL) 13 July 1972 see claims --	1-9	Y	US, A, 3790423 (F.B. JONES) 5 February 1974 see claims --	1-9	Y	US, A, 3843611 (R.W. CAMPBELL) 22 October 1974 see claims --	1-9	Y	Chemical Abstract, volume 78, no. 8, 26 February 1973, (Columbus, Ohio, US), see page 64, abstract 44934x, & JP, A, 7229451 (TORAY INDUSTRIES, INC.) 2 August 1972 ----	1-9
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[*] Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published 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; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family																	
IV. CERTIFICATION																	
Date of the Actual Completion of the International Search 9th October 1990	Date of Mailing of this International Search Report 06. 11. 90																
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Mme N. KUIPER																

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9003030

SA 38192

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 23/10/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A- 2116379	13-07-72	US-A- 3833547	03-09-74
		DE-A- 2152267	27-04-72
		GB-A- 1374275	20-11-74
		US-A- 3792083	12-02-74
US-A- 3790423	05-02-74	None	
US-A- 3843611	22-10-74	None	