Polyamide compositions containing Reissert units can be formed by the reaction of an open chain bis Reissert compound or a mono Reissert compound with a diamine and a diacid chloride.

6 Claims, No Drawings
POLYAMIDE CONTAINING REISSERT UNIT(S)

BACKGROUND OF THE INVENTION

Polyamides are an important and well known class of polymers used as fibers (textile and industrial) as well as in construction and are formed by the condensation polymerization of a diamine and a dicarboxylic acid. Poly(hexamethylene adipamide) was the first synthetic fiber produced industrially on a large scale by Carothers with the trade name nylon-66 and it has the following structure.

\[
H\left(-NH-\left(CH_2\right)_{10}-NH\right)\left(-CO-\left(CH_2\right)_{4}-CO\right)=\text{OH}
\]

Nylon-66 is one of the important polyamides with an excellent fiber and thermoplastic properties. For example, nylon-66 is silk like and has displaced both natural silk and cotton from the market. In addition, it can be readily dyed or pigmented and has good texturizing properties. The dyeability can be varied within wide limits by copolymerization with monomers containing acidic or basic groups, by end group variation, or by grafting. Such applications in various areas other than the textile industry has also been very well documented in literature. Polyamides containing aliphatic cyclic structures in the polymer chain are somewhat superior to the acyclic polyamides in terms of thermal stability, whereas aromatic polyamides have greatly improved thermal stability compared to aliphatic polyamides. However, most of these polyamides are soluble only in H2SO4, formic acid and m-cresol. Thus, the net range of studies of these polymers in solution is limited.

An object of the present invention is to utilize open chain Reissert compounds to improve the properties of polyamides. U.S. Pat. No. 4,929,713 reports the synthesis of open chain poly(Reissert compounds) by the aromatic diazide and primary amine, in the presence of cyanide and bisulfite, followed by reaction of the product with an aliphatic diacid chloride. It does not suggest use of Reissert chemistry for the modification of polyamides.

SUMMARY OF THE INVENTION

The present invention relates to the modification of polyamides (e.g., nylon 6,6) by the incorporation of one or more open chain Reissert units therein. The incorporation can be by manner of end capping the polyamide, for formation of a block copolymer comprising nylon and Reissert units, or by the formation of a random copolymer containing such units.

Copolymers, either random or block copolymers, containing polyamide and Reissert units can be synthesized by reaction of the type of α-amino nitrile described in U.S. Pat. No. 4,929,713 which has the structure

\[
NC-\text{CH}Ar-\text{CHCN,}
\]

where R is alkyl, e.g., lower alkyl, with a diazo chloride and a diamine. The diazo chloride can have the general formula ClC(O)R'C(O)Cl, where R1 can be alkylene, e.g., C4 alkylene, and the diamine can be of the formula H2NR2NH2, where R2 can also be alkylene, such as C4 alkylene. The reaction conditions used can be the type of reaction conditions analogously used to form conventional polyamide compositions (e.g., a chlorinated hydrocarbon solvent and an amine acid acceptor, such as triethylamine). Random copolymer formation is favored when the diacid chloride is added to the α-amino nitrile followed by the addition of the diamine. The reaction favors block copolymer formation when the diacid chloride is added to the mixture of α-amino nitrile and diamine.

The polymers that are formed in accordance with the present invention comprise units containing the Reissert structure (R and R1 being as defined above):

\[
\begin{align*}
\text{R} & \quad \text{NH-}\text{R}^1 \\
\text{CN} & \quad \text{CN} \\
\text{R}^3 & \quad \text{R}^4
\end{align*}
\]

and units containing polyamide units (R1 and R2 as defined above):

\[
\begin{align*}
\text{R} & \quad \text{NH-}\text{R}^2 \\
\text{CN} & \quad \text{CN} \\
\text{R}^3 & \quad \text{R}^4
\end{align*}
\]

where R1 is alkyl, for example, ethyl, and R4 can also be alkyl, for example methyl.

End capped oligomers or polymers will have the following general structure, for example (R1 to R4 being as earlier defined):

\[
\begin{align*}
\text{CN} & \quad \text{CN} \\
\text{R}^3 & \quad \text{R}^4
\end{align*}
\]

The foregoing invention is further illustrated by the Examples which follow.

EXAMPLE 1

Synthesis of Nylon-6,6 (Reference: Practical Macromolecular Organic Chemistry, K. J. Ivin, ed., Harwood Academic Publishers, New York, 1984, p 258): To a mechanically stirring solution of 1,6-hexanodiamine (49.9 mmole, 5.7982 gm, weighed under N2 atm), and triethylamine (101 mmole, 15.3 mL) in CHCl3 (100 mL, dry, alcohol free) was added adipoyl chloride (49.9 mmole, 9.1321 gm in CHCl3 (20 mL) under dry conditions in less than thirty seconds. This reaction was very exothermic and needed double condensers cooled by ice-water circulation. However, the reaction mixture was not cooled to suppress the reaction rate. The reaction mixture was left stirring overnight, and then excess CHCl3 and triethylamine were removed by rotary evaporation. The residue was poured into water (IL) and stirred at room temperature for five hours. The white solid obtained by filtration was treated with 1M HCl, filtered, washed with excess of water, and dried (1 mm/45°C, overnight), 7.52 gm (67%). [9]=0.51 D/L/gm (25°C, m-cresol). TGA: 10% wt loss (air)=380°C. DSC: Tg=61°C, Tm=251°C. 1H NMR (CF3COOD+TMS): 811.69 (s, CF3COOH+NH+--
EXAMPLE 2

Triblock Copolymer:
To a mechanically stirring solution of 1,6-hexanedi-
mine (31.87 mole, 3.6475 gm, weighed under N2
H2O), 3.59(s,2XN—CH2), 2.81(s,2XCOCH2), 1.95,
double condensers cooled by ice-water circulation.
However, the reaction mixture was not cooled to sup-
press the reaction rate. The reaction mixture was left
stirring overnight, and then excess CHC13 and triethyl-
amine were removed by rotary evaporation. The resi-
due was poured into water (1L) and stirred at room
temperature for five hours. The white solid obtained by
filtration was treated with 1M HCl, filtered, and dried
(1 mm/45° C., overnight), 7.02 gm (68%), [%]=0.57
dL/gm (25° C., m-cresol). TGA: 10% wt loss (air)=320' C. DSC: Tg=59° C., Tm=248° C. 1H NMR
(CH3COOD+TMS): Integration calculations for
aromatic and acidic protons to aliphatic protons revealed
that the polymer contained 37% Reissert units and 62%
nylon-6,6 units.

EXAMPLE 3

Triblock Copolymer:
To a mechanically stirring solution of 1,6-hexanedi-
mine (44.725 mole, 5.1975 gm, weighed under N2 atm),
a,a'-dicyano-a,a'-bis(N-methylamino)-p-xylene
(17.895 mmole, 3.8344 gm), and triethylamine (110
mmole, 15.3 mL) in CHC13 (100 mL, dry, alcohol free),
was added adipoyl chloride (49.282 mmole, 9.02 gm
in CHC13 (50 mL), under dry conditions in less than thirty
seconds. This reaction was very exothermic and needed
double condensers cooled by ice-water circulation.
However, the reaction mixture was not cooled to sup-
press the reaction rate. The reaction mixture was left
stirring overnight, and then excess CHCl3 and triethyl-
amine were removed by rotary evaporation. The resi-
due was poured into water (1L) and stirred at room
temperature for five hours. The white solid obtained by
filtration was treated with 1M HCl, filtered, and dried
(1 mm/45° C., overnight), 5.29 gm (50%), [%]=0.55 dL/gm (25° C., m-cresol). TGA: 10% wt loss
(air)=340° C. DSC: Tg=59° C., Tm=250° C. 1H NMR
(CH3COOD+TMS): Integration calculations for
aromatic and acidic protons to aliphatic protons revealed
that the polymer contained 32% Reissert units and 68%
nylon-6,6 units. 1H NMR (DMF - d6): Integration
calculations for aromatic and acidic protons to aliphatic
protons revealed that the polymer contained 3.5% Reissert units and 96.5% ny-
lon-6.6 units.

EXAMPLE 4

Open chain poly(Reissert compound):
U.S. Pat. No. 4,929,713 in Examples 1–2 illustrate
synthesis of this composition.

EXAMPLE 5

Nylon 6,6 end capped with Reissert compound:
To a mechanically stirring solution of 1,6-hexanedi-
mine (46.92 mmole, 5.4524 gm, weighed under N2 atm),
and 1-cyano-1-(N-methylamino)propane (1.902 mmole,
0.1870 gm), triethylamine (110 mmole, 15.3 mL) in
CHCl3 (100 mL, dry, alcohol free), was added adipoyl
chloride (47.87 mmole, 8.7616 gm) in CHCl3 (20 mL)
was added under dry conditions in less than twenty
seconds. This reaction was very exothermic and needed
double condensers cooled by ice-water circulation.
However, the reaction mixture was not cooled to sup-
press the reaction rate. The reaction mixture was left
stirring overnight, and then excess CHCl3 and triethyl-
amine were removed by rotary evaporation. The resi-
due was poured into water (1L) and stirred at room
temperature for five hours. The white solid obtained by
filtration was treated with 1M HCl (1L), water (excess),
methanol (1L), methanol (1L) filtered, and dried (1
mm/45° C., overnight), 7.02 gm (68%), [%]=0.57
dL/gm (25° C., m-cresol). TGA: 10% wt loss (air)=320° C. DSC: Tg=59° C., Tm=248° C. 1H NMR
(CH3COOD+TMS): Integration calculations for
aromatic and acidic protons to aliphatic protons revealed
that the polymer contained 3.5% Reissert units and 96.5% ny-
lon-6,6 units.
EXAMPLE 8

Nylon 6,6 end capped with Reissert compound:

To a mechanically stirring solution of triethylenamine (110 mmole, 16 mL) in dimethylformamide (25 mL) the following two solutions were added dropwise simultaneously over a fifteen minute period at 5°-10°C: (a) adipoyl chloride (50.0 mmole, 9.1520 gm) in dimethylformamide (25 mL); and (b) 1,6-hexanediarnine (50.0 mmole, 5.80 gm), and 1-cyano-1-(N-methylamino)propane (100 mmole, 9.815 gm) in dimethylformamide (25 mL). The reaction mixture was stirred for two days at room temperature and then poured into water (3L). The white solid obtained by filtration was washed with excess water and methanol and was dried (1 mm/45°C, overnight), 2.70 gm. [\(\eta\)] = 0.13 dL/gm (25°C, m-cresol). TGA: 10% wt loss (air) = 370°C. DSC: Tm = 226°, 235°C. 1H NMR (CF3COOD+TMS): Integration calculations for acidic protons to aliphatic protons revealed that the polymer contained 6% Reissert units and 94% nylon-6,6 units. The filtrate was extracted with EtOAc (3x300 mL). The organic layer was consecutively washed with 8% EC] (3x300 mL), water (3x300 mL), saturated NaHC03 (3x300 mL), water (3x300 mL), and then 1,6-hexanediamine (34.392 mmole, 3.9967 gm) in CHCl3 (20 mL) under dry conditions in a two minute period at 5°-10°C. This yellowish solution was stirred for fifteen minutes and then 1,6-hexanediame (34.392 mmole, 3.9967 gm) in CHCl3 (50 mL) was added. The reaction mixture was left stirring overnight, and then excess CHCl3 and triethylamine were removed by rotary evaporation. The residue was poured into water (IL) and was stirred at room temperature for five hours. The white solid obtained by filtration was consecutively treated with aqueous HCl (IL, pH of about 3), water-acetone (1:1, IL), water (IL), filtered, and dried (1 mm/45°C, overnight), 6.0 gm. [\(\eta\)] = 0.11 dL/gm (25°C, m-cresol). TGA: 10% wt loss (air) = 260°C. DSC: Td = 104°C. 1H NMR (CF3COOD+TMS): Integration calculations for aromatic and acidic protons to aliphatic protons revealed that the polymer contained 57% Reissert units and 43% nylon-6,6 units.

The Table given below gives some of the characteristics which were determined for the structures realized from the foregoing synthesis procedures. In the Table the following letters denote the following respective structures:

- A—Nylon 6,6: H[\(\text{NH-CH}_2\text{CN-CH(CN)-N(CH}_3\text{)}\text{CO-}-(\text{CH}_2\text{)}_4\text{-CO}\]n
- B—Triblock copolymer of Reissert (x) and nylon, 6,6 (y) repeating units:
- C—Open chain poly(Reissert compound):
- D—Nylon 6,6-end capped with Reissert compound:
- E—Random copolymer:

In each of the above where Ar appears it is meant to depict a 4,4'-substituted phenyl ring. Structure A is set forth as a control. Structure C depicts the type of open chain poly(Reissert compound) covered by U.S. Pat. No. 4,929,713 in which methyl substitution is on the nitrogen atom in the backbone. Structures B, D and E are intended to illustrate certain embodiments of the present invention.
TABLE

<table>
<thead>
<tr>
<th>Structure</th>
<th>Solubility</th>
<th>Viscosity (dL/g, in m-Cresol)</th>
<th>TGA (air)</th>
<th>TGA (DSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ratio (x:y)</td>
<td>% wt</td>
<td>°C</td>
</tr>
<tr>
<td>A</td>
<td>Cl(_2)CHCO(_2)H</td>
<td>0.51</td>
<td>0:100</td>
<td>0:100</td>
</tr>
<tr>
<td>B</td>
<td>Cl(_2)CHCO(_2)H</td>
<td>0.50</td>
<td>36:64</td>
<td>32:68</td>
</tr>
<tr>
<td>C</td>
<td>DMF, DMSO, m-Cresol</td>
<td>0.15</td>
<td>100:0</td>
<td>100:0</td>
</tr>
<tr>
<td>D</td>
<td>m-Cresol</td>
<td>0.57</td>
<td>2:98</td>
<td>3:5:96:5</td>
</tr>
<tr>
<td>E</td>
<td>DMF, MeOH</td>
<td>0.16</td>
<td>34:66</td>
<td>43:57</td>
</tr>
<tr>
<td>F</td>
<td>DMF, MeOH</td>
<td>0.11</td>
<td>34:66</td>
<td>57:43</td>
</tr>
</tbody>
</table>

*The polymer (200 mg) dissolved to the extent of over 95% in hot m-cresol (20 ml). The solution was cooled to room temperature and viscosities were run at room temperature.

The solid state \(^1\)C NMR spectrum clearly showed the incorporation of the Reissert group. However, copolymer ratio calculations were not accurate due to overtone bands overlapping as well as inherent inaccuracy of integration values.

Decomposition of this polymer was noted in TFA with time.

We claim:

1. A modified polyamide composition which comprises: polyamide units of the formula \(\text{--[NH--R}\_2\text{--N--H--CO--R}\_1\text{--CO]}\)-where \(R_1\) and \(R_2\) are alkylenes, and at least one open chain Reissert unit of either the formula

\[
\begin{align*}
\text{R} & \quad \text{R} \\
\text{CN} & \quad \text{CN} \\
\text{N--CH--Ar--CH--N--CO--R}\_1\text{--CO} & \quad \text{N--CH--N--CO--R}\_1\text{--CO}
\end{align*}
\]

where \(R_3\) and \(R_4\) are alkyl and \(R_1\) is alkylylene or the formula

\[
\begin{align*}
\text{R} & \quad \text{R} \\
\text{CN} & \quad \text{CN} \\
\text{N--CH--Ar--CH--N--CO--R}\_1\text{--CO} & \quad \text{N--CH--N--CO--R}\_1\text{--CO}
\end{align*}
\]

where \(Ar\) is phenylene, \(R\) is alkyl and \(R_1\) is alkylylene or the formula

\[
\begin{align*}
\text{R} & \quad \text{R} \\
\text{CN} & \quad \text{CN} \\
\text{N--CH--Ar--CH--N--CO--R}\_1\text{--CO} & \quad \text{N--CH--N--CO--R}\_1\text{--CO}
\end{align*}
\]

where \(R_3\) and \(R_4\) are alkyl and \(R_1\) is alkylylene.

2. A composition as claimed in claim 1 wherein the polyamide unit is nylon 6,6.

3. A composition as claimed in claim 1 wherein \(R_1\) is \(C_6\) alkylylene.

4. A composition as claimed in claim 1 wherein \(R_1\) is \(C_6\) alkylylene.

5. A composition as claimed in claim 1 wherein \(R_3\) is ethyl.

6. A composition as claimed in claim 1 wherein \(R_4\) is methyl.