Polyurethaneureas, polyurethaneurea fibre and preparation thereof

The invention relates to a process for preparing polyurethaneureas, novel polyurethaneureas, a process for preparing elastane fibre composed of polyurethaneureas and the elastane fibre obtainable by the process. The polyurethaneureas are based on an aliphatic or cycloaliphatic diisocyanate, a polymeric diol, an aliphatic or cycloaliphatic diamine and optionally a secondary aliphatic amine. The elastane fibre combines excellent mechanical properties with good light fastness.

Elastanes are mono- or multifil continuous yarns composed of at least 85% by weight of segmented poly(urethane)s or poly(urethaneurea)s. The fibre-forming polymers have a segmented structure; that is, they are composed of "crystalline" and "amorphous" blocks ("hard segments" and "soft segments"). The hard segments, owing to their "crystallinity", act as fixed points of the network and hence determine the strength of the shaped articles or fibres prepared from the polymers. By contrast, the soft segments, the glass transition temperature of which has to be below the use temperature, determine the elasticity of the elastanes.

Such elastanes are customarily prepared by polyaddition of long-chain dihydroxy compounds (macrodiols) with diisocyanates and low molecular weight dihydroxy or diamino compounds as chain extenders. High grade elastane filaments (also known as spandex) are prepared using poly(urethaneurea)s obtained by chain extension with diamines, since, compared with the diol-extended poly(urethane)s, they have (because of a larger number of hydrogen bonds between the polymer chains) a high hard-segment melting point on the one hand and excellent mechanical-elastic properties on the other. Elastane fibres are customarily produced by spinning solutions of these segmented poly(urethaneurea)s in highly polar solvents such as dimethylformamide and dimethylacetamide by means of the so-called dry spinning process or the wet spinning process or alternatively, without use of a spinning solvent, by spinning from the melt.

According to the prior art, elastanes prepared from aromatic diisocyanates (especially 4,4'-diphenylmethane diisocyanate [MDI]), polymeric diols and also mixtures of diamines and monoamines have found the widest use. However, these materials have the serious disadvantage that they yellow and lose their mechanical properties on exposure to light, or especially UV rays, and also on contact with chlorine or nitrogen

oxides. For this reason, commercially available elastanes based on aromatic diisocyanates have added to them light and chlorine stabilizers which, however, have only a limited usefulness, in terms of both time and quality, and also increase the manufacturing costs of the elastanes.

The patent DE 2858773 C2 describes polyurethanes obtained by reaction of macrodiols having average molecular weights of 800 to 4000, 1,4-cyclohexane diisocyanate having a trans isomer content of at least 95% and hydrazine as chain extender. However, the fibres obtained by the process described have unsatisfactory properties for elastanes, especially insufficient mechanical properties, for example a poor tenacity. In addition, the chain extension is effected using the toxicologically problematical hydrazine. The spinning solutions obtained have a comparatively low solids content at 15% by weight, which is disadvantageous both economically and ecologically, since the removal and recovery of the spinning solvents is very costly.

The OPI document DE-A-1 955 725 describes elastomeric block polyurethanes formed from bifunctional, low molecular weight polymers having terminal active hydrogen atoms (such as for example polyethers), organic diisocyanates and diamines as principal components. The diisocyanates used are 4,4'-methylenebiscyclohexyl diisocyanate, 4,4'-isopropylidenebiscyclohexyl diisocyanate, 4,4'-oxybiscyclohexyl diisocyanate or 1,4-cyclohexyl diisocyanate. However, the elastanes obtained from these block polyurethanes have unsatisfactory mechanical properties (especially a low tenacity), which is probably attributable to the excessively low molecular weight of the polymers obtained. In addition, the elastanes are prepared using trans,trans-enriched cycloaliphatic diisocyanates, which are very costly to prepare.

The British Patent GB 1 110 868 describes elastic polyurethane fibres which are obtained using organic diisocyanates and also diamines each containing 4,4'-alkylidenebiscyclohexyl radicals. However, the mechanical properties (especially the tenacity) of these materials are unsatisfactory; the spinning solutions used, moreover, have a comparatively low solids content (not more than 26% by weight), which makes processing by the dry spinning process uneconomical.

In general, it can be stated that elastane materials based on purely aliphatic materials have not succeeded in becoming established in industrial practice because of physico-chemically or process-based disadvantages (compare also: Ullmann's Encyclopedia of Industry Chemistry, A 10, p. 611 (1987)). Solely the addition of 1,6-hexane

diisocyanate as spin viscosity modifier in the synthesis of elastane fibres comprising, inter alia, aromatic diisocyanates as hard segment and polyesters as soft segment has hitherto led to any use of aliphatic diisocyanates (compare also: U.S. Pat. No. 3,377,308).

It is an object of the present invention to provide a process for preparing elastane fibres which are the equal of commercially available elastanes in their mechanical properties, which were prepared using aromatic diisocyanates and which, without addition of stabilizers, possess good ageing stability under the agency of light and which, moreover, exhibit good chlorine stability and also high resistance to discoloration due to gases.

It is a further object of this invention to provide isophorone diisocyanate based elastane materials which likewise are the equal of commercially available elastanes in their mechanical properties, which were prepared using aromatic diisocyanates and which, without addition of stabilizers, possess good ageing stability under the agency of light and which, moreover, exhibit good chlorine stability and also high resistance to discoloration due to gases.

It is a further particular object to provide elastane fibres, or a process for providing elastane fibres, which are characterized by a low residual extension value on the part of the elastic fibres obtained, a simultaneously high extension potential of at least 400% and a tenacity of above 0.9cN/dtex and HDT (heat distortion temperature) values of at least 170°C.

This object is achieved by devising and providing the hereinbelow more particularly described process of the invention.

It was found that a multistage process can be used to provide polyurethaneureas which have a weight average molecular weight of especially 50,000 to 400,000 (determined by gel permeation chromatography and comparison with polystyrene standards) and from which it is possible to prepare elastanes which exhibit the above-described desired combination of properties. It is surprising that elastane fibres having particularly good mechanical properties and very good thermal stability are obtained on preparing the spinning solution for use in the stepwise process by, in the prepolymer preparation, initially reacting only part of the diisocyanate with the polymeric diol and adding the remainder of the diisocyanate immediately prior to the

chain-extending step. It was further found that isophorone diisocyanate especially is useful as the basis for obtaining elastane fibres which exhibit the above-described desired combination of properties.

The invention accordingly provides a multistage process for preparing polyurethaneureas by preparing a prepolymer in solution or in the melt and then chain-extending the prepolymer in solution or in the melt, which comprises a first step of preparing the prepolymer (which is also referred to as "isocyanate-capped glycol") from

A) a polymeric diol of the general structure HO-Q-OH,
where Q is
a radical: $-[(CH_2)_nO]_m-$ or $-[(CH_2)_pCH(CH_3)CH_2O]_o-$
wherein n is a number from 2-10, m is a number from 1-150, o is a number from 1-150 and p is a number from 0-2,

a polyester radical prepared on the basis of adipic, sebacic, succinic or dodecanedioic acid or mixtures of these acids with diols of the general structure

HO-A-OH,

where A is a radical: $-[(CH_2)_r(CR^1R^2)_qCH_2)_s]-$,
wherein r is a number from 1-5, q is a number from 0-1,
s is a number from 0 to 5
and R^1 and R^2 are independently -H or $-CH_3$,
it being possible to use not only mixtures of these diols but also a single diol,

a polycaprolactone radical, preferably having a molecular weight of 500 to 5000,

or a polycarbonate radical such as a poly(pentane-1,5-carbonate) or poly(hexane-1,6-carbonate) radical, preferably having a molecular weight of 500 to 5000,

or a mixture of such polymeric diols A), and also

B) an aliphatic or cycloaliphatic, especially cycloaliphatic, diisocyanate such as 1,6-hexane diisocyanate (HDI), 1,4-butane diisocyanate (BDI), 1,4-cyclohexyl diisocyanate (CDI), 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI), isophorone diisocyanate (IPDI), tetramethylxylylene diisocyanate (TMXDI) or dimeryl diisocyanate (DDI) or mixtures of these diisocyanates
having an NCO:OH ratio of 1.3 to 3.0, preferably of 1.5 to 2.3
either in a solvent such as dimethylformamide (DMF), dimethylacetamide (DMAc) or N-methylpyrrolidine (NMP) or some other dipolar aprotic solvent or in the melt,
by heating the components, after they have been mixed, to 30°C to 100°C, preferably 40°C to 80°C, in the case of the use of solvents, or to 60°C to 200°C, preferably 80°C to 150°C, in the case of a reaction in the melt, for a duration of 0.5 to 5 hours, preferably 1 to 5 hours, with stirring,

a subsequent second step at a temperature of 0°C to 100°C of mixing further diisocyanate B) into the reaction mixture (prepolymer of the first stage from A) and B)) so that the total ratio of NCO:OH of the ingredients A and B is 1.7 to 6.0,
and a third step of reacting the chain extension
either in the presence of a solvent such as dimethylformamide (DMF), dimethylacetamide (DMAc) or N-methylpyrrolidine (NMP) or other dipolar aprotic solvents both batchwise with stirring and continuously with careful mixing at a temperature of -20°C to 100°C, preferably 0°C to 80°C
or in the melt at a temperature of 100°C to 250°C using

C) an aliphatic or cycloaliphatic, especially cycloaliphatic, diamine selected from the group consisting of ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, 1,4-diaminobutane, 1,5-diaminopentane, 1,3-diaminocyclohexane, diaminomethylcyclohexane, isophoronediamine or mixtures of such diamines and triamines such as diethylenetriamine and optionally using

D) a primary or secondary, aliphatic and/or cycloaliphatic amine such as diethylamine, ethanolamine, di-n-butylamine or cyclohexylamine, especially diethylamine, ethanolamine, di-n-butylamine,

the molar ratio of diamine to amine based on amino groups being 100:0 to 100:20, preferably to 100:10, using a molar amine excess based on reactive isocyanate units of 0 to 25%, preferably 0 to 15%.

Preference is given to a process in which the polymeric diol A) has the general structure HO-Q-OH,
where Q is
a radical: $-[(CH_2)_nO]_m-$
wherein n is 4, m is a number from 10-70.

Preference is also given to a process in which the polymeric diol A) has the general structure HO-Q-OH,
where Q is a polyester radical prepared on the basis of adipic, sebacic, succinic or dodecanedioic acid with diols of the general structure:

HO-A-OH

where A is a radical: $-[(CH_2)_r(CR^1R^2)_q(CH_2)_s]-$,
wherein r is a number from 1-5, q is a number from 0-1, s is a number from 0 to 5 and R^1 and R^2 are independently -H or $-CH_3$.

The preferred polymeric diols can also be used in any desired mixture.

The aliphatic or cycloaliphatic diisocyanate B) is especially 1,4-butane diisocyanate (BDI), 4,4'-dicyclohexylmethane diisocyanate ($H_{12}MDI$), isophorone diisocyanate (IPDI) or a mixture thereof.

Preference is also given to a process which is characterized in that the mixing and reacting of the further diisocyanate B) with the reaction mixture in the second stage is effected at a temperature of 20°C to 80°C, so that the total ratio of NCO:OH is 1.7 to 5.0.

The chain extension in the third stage is especially carried out in such a way that the molar ratio of isocyanate structures to Zerevitinov-active hydrogen atoms of the amines is 1.25:1 to 1:1.25.

The invention further provides polyurethaneureas based on

A) a polymeric diol of the general structure HO-Q-OH,
where Q is
a radical: $-[(CH_2)_nO]_m-$ or $-[(CH_2)_pCH(CH_3)CH_2O]_o-$
wherein n is a number from 2-10, m is a number from 1-150, o is a number from 1-150 and p is a number from 0-2,

a polyester radical prepared on the basis of adipic, sebacic, succinic or dodecanedioic acid with diols of the general structure

HO-A-OH,

where A is a radical: $-[(CH_2)_r(CR^1R^2)qCH_2)_s]-$,
wherein r is a number from 1-5, q is a number from 0-1,
s is a number from 0 to 5
and R^1 and R^2 are independently -H or $-CH_3$,
it being possible to use not only mixtures of these diols but also a single diol,

a polycaprolactone radical or a polycarbonate radical such as poly(pentane-1,5-carbonate) diol or poly(hexane-1,6-carbonate) diol
or a mixture of such polymeric diols A), and also

B) isophorone diisocyante (IPDI)

C) an aliphatic or cycloaliphatic diamine selected from the group consisting of ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, 1,4-diaminobutane, 1,5-diaminopentane, 1,3-diaminocyclohexane, diaminomethylcyclohexane, isophoronediamine or mixtures of such diamines and triamines such as diethylenetriamine and optionally using

D) a primary or secondary, aliphatic and/or cycloaliphatic amine such as diethylamine, ethanolamine, di-n-butylamine or cyclohexylamine.

The invention further provides a process for preparing elastane fibre, filament or yarn (hereinafter simplified to elastane yarn) by spinning a polyurethaneurea solution by the dry spinning process, characterized in that a spinning solution comprising a polyurethaneurea obtainable from the abovementioned process according to the invention is spun through a spinnerette into a chimney, the solvent is removed at a chimney temperature of 150°C to 350°C, preferably 180°C to 250°C, and a spinning

gas temperature of 150°C to 380°C, preferably 220°C to 360°C, the solidified yarn is taken off, optionally drawn, optionally set, spin finished and wound up on bobbins.

The invention further provides a process for preparing elastane fibre, filament or yarn by spinning a polyurethaneurea solution by the wet spinning process into a coagulation bath with fibre formation through coagulation, removing the solvent in the coagulation bath, washing the yarn product, preferably in water, drying the yarn, optionally drawing, optionally setting, spin finishing and winding up on bobbins, characterized in that the spinning solution used comprises a polyurethaneurea obtainable from the abovementioned process according to the invention.

Prior to the spinning of the spinning solution by wet spinning or dry spinning, the polyurethaneurea solution can optionally and additionally have added to it additives such as: antistats, for example salts of organic acids or quaternary ammonium salts, lubricants, for example metal salts of long-chain carboxylic acids, especially of oleic acid, stearic acid and palmitic acid, particularly preferably magnesium stearate, dyes, pigments, for example TiO_2, stabilizers or dyeing auxiliaries.

The invention further provides an alternative melt spinning process for preparing elastane fibre by preparing a polyurethaneurea melt by the prepolymer process and spinning the polymer melt obtained, characterized in that the polyurethaneurea melt is prepared by the abovementioned process according to the invention, the polymer melt is spun directly following its preparation, and the resulting elastane fibre is cooled, optionally drawn, spin finished and wound up.

In a preferred melt spinning process for preparing elastane fibre, the polymer melt obtained following chain extension is initially cooled and granulated instead of being directly spun and the resulting polymer granules are melted and melt spun into elastane yarn.

Yarn is melt spun especially at a temperature of 180°C to 270°C, preferably at a jet temperature of 190-250°C. The resulting filaments are cooled, for example by quenching with air. The take-off speed of the yarn is especially, depending on its fineness (linear density), within the range from 100 m/min to 1000 m/min, preferably 200 m/min to 800 m/min.

Preference is given to a process wherein the polyurethaneurea melt, after lubricants and stabilizers have been mixed in, is spun without further intermediate steps, at a temperature of 180-250°C and at a speed of 200-1000 m/min in plural-end form.

The filaments are then for example continuously, i.e. without intermediate laydown, drawn. Preference is given to cold drawing at a temperature of 20-50°C to a draw ratio of 1.05 to 5.0, preferably of 1.1-2.5. The filaments then pass through a relaxation zone and have a spin finish customary for elastanes applied to them, before being wound up at a speed of 200-1200 m/min, preferably 400-1000 m/min.

The spinning processes of the invention make it possible to produce elastic yarns in monofil and multifil form. Preferably, melt spinning is used to produce monofilaments, and wet spinning and dry spinning are used to produce multifilaments.

The wound yarn obtained by the melt spinning process is then optionally subjected to a thermal aftertreatment (tempering), especially at a temperature of 50-120°C, preferably 60-100°C, for 1 hour to 96 hours, preferably for 16 hours to 48 hours.

This tempering can be carried out not only in vacuo but also in air or inert gases; tempering in air is preferred.

The intensity of tempering depends on the basic chemical and physical structure of the yarn and on its fineness (linear density). The tempering conditions must be chosen in such a way that, following such a treatment, packages having adequate unwinding characteristics for further processing are present.

The elastic yarn prepared by the process of the invention also forms part of the subject-matter of the invention and is characterized by low residual extensibility of not more than 35%, preferably 5-35%, coupled with a simultaneously high ultimate tensile stress extension of not less than 400%, especially 400-650%. The force/extension and hysteresis characteristics typical of conventional elastanes are observed. Tenacities > 0.9 cN/dtex are obtained predominantly in the case of the preferred fibres. This is an essential prerequisite for the preparation of low denier yarn. Particularly preferred elastane yarn has a linear density of 17-80 dtex.

More particularly, the elastane fibres prepared by the process of the invention possess high stability under thermal stress and plastic flow as reflected in an HDT (heat distortion temperature) value of above 165°C.

The invention further provides elastane yarn obtainable according to any of the processes of the invention.

The elastic filaments are very useful alone or in combination yarns together with other filaments comprising for example polyamide, wool, cotton and polyester for processing into textile goods, for example by means of warp knitting, circular knitting and flat knitting. As well as for use in hosiery, the elastic yarn prepared by the process of the invention is because of its high thermal stability particularly useful for application in fields which require a specific heat-settability, for example underwear, corsetry, sportswear, outerwear and cover fabrics.

The invention also provides for the use of the elastane yarn of the invention for preparing yarn especially combination yarn with other synthetic and nonsynthetic yarn fibre or filament and for preparing textile fabrics, such as consecutive course formation knits, wovens or simultaneous course formation knits.

Examples

Example 1:

2395 g of polytetramethylene glycol (hydroxyl number 56.0) are devolatilized at 130°C for 1 hour. Sufficient isophorone diisocyanate is added for an NCO:OH ratio of 1.85:1. This is followed by stirring at 130°C for 4 h. Thereafter, sufficient isophorone diisocyanate is added at 50°C for a total NCO:OH ratio of 2.85:1. Following addition of 1350 g of dimethylacetamide, 80% of this solution are admixed with a mixture of 304 g of isophoronediamine and 1.16 g of di-n-butylamine (as 5.2% strength dimethylacetamide solution) to produce a stable spinning solution having a viscosity of about 80.0 Pas.

Example 2:

The prepolymer is synthesized as shown in Example 1, except that 47,000 g of polytetramethylene glycol (hydroxyl number 56.0) are used. In a mixer, 3 parts per minute of the prepolymer are diluted with 4.5 parts of dimethylacetamide and continuously metered into 2.5 parts of a solution consisting of 34.92 g of isophoronediamine and 0.135 g of di-n-butylamine, dissolved as 14% strength solution in dimethylacetamide to form a stable spinning solution having a viscosity of about 76.0 Pas.

Example 3:

The prepolymer is synthesized as described under Example 1, except that the polytetramethylene glycol having a hydroxyl number of 56.0 is replaced by the corresponding amount of a polytetramethylene glycol having a hydroxyl number of 39.3. 75.5% by weight of the dimethylacetamide-diluted prepolymer solution are poured into a 6.8% strength suspension of 256.3 g of isophoronediamine, 0.98 g of di-n-butylamine and 151 g of CO_2 in dimethylacetamide and stirred in until there is no further increase in the viscosity. The result is a stable spinning solution having a viscosity of about 87.3 Pas.

Example 4:

The prepolymer is synthesized as described under Example 1, except that the polytetramethylene glycol having a hydroxyl number of 56.0 is replaced by the corresponding amount of a polyester prepared from adipic acid, 1,6-hexanediol, 1,4-butanediol and neopentyl glycol having a hydroxyl number of 33.9. The NCO:OH ratio is 2.2:1. The reaction time is 105 min. Thereafter, sufficient isophorone diisocyanate is added at 50°C for a total NCO:OH ratio of 3.2:1. 75.4% by weight of a dilution of the prepolymer solution with 1452 g of dimethylacetamide are poured into a 6.75% strength suspension of 258.5 g of isophoronediamine, 0.49 g of di-n-butylamine and 137 g of CO_2 in dimethylacetamide and stirred in until there is no further increase in the viscosity. The result is a stable spinning solution having a viscosity of about 77.0 Pas.

Example 5:

The prepolymer is synthesized as described under Example 4, except that the macrodiol used is a 7:3 mixture of a polyester prepared from adipic acid, 1,6-hexanediol, 1,4-butanediol and neopentyl glycol having a hydroxyl number of 33.9 and a polytetramethylene glycol having a hydroxyl number of 56.0. The NCO:OH ratio is 2.2:1. The reaction time is 180 min. Thereafter, sufficient isophorone diisocyanate is added at 50°C for a total NCO:OH ratio of 3.2:1. 66.7% of the dilution of the prepolymer solution with 1642 g of dimethylacetamide are poured into a 7.40% strength suspension of 289.8 g of isophoronediamine, 0.55 g of di-n-butylamine and 153 g of CO_2 in dimethylacetamide and stirred in until there is no further increase in the viscosity. The result is a stable spinning solution having a viscosity of about 76.0 Pas.

Comparative Example 1:

The prepolymer is synthesized as in Example 2, except that 4,4'-methylenediphenyl diisocyanate is used instead of isophorone diisocyanate. The NCO:OH ratio is 1.65:1. The reaction time is 4 h at 80°C. The result following chain extension with ethylenediamine is a spinning solution having a viscosity of about 100 Pas.

Comparative Example 2:

Synthesis of the prepolymer as in Comparative Example 1, except that a polyester prepared on the basis of adipic acid, 1,6-hexanediol and neopentyl glycol and having a hydroxyl number of 56 is used instead of polytetramethylene glycol. The result following chain extension with ethylenediamine is a stable spinning solution having a viscosity of about 80.0 Pas.

Description of test methods used hereinbelow:

- Exposure to light in accordance with DIN 54004
- NOx in accordance with DIN 54025.

The spinning solutions prepared according to the preceding examples were used for spinning trials in a dry spinning plant. The dry spinning chimney has a total length of 5300 mm and a diameter of 270 mm. The take-up unit consists of a winder from IWKA with two separate godets which can be operated both in the tension mode and in the relaxation mode. The actual winding unit can be handled at up to speeds of 1200 m/min. This dry spinning unit permits a plural end spinning of mono- and of multifilaments.

The production conditions for dry spinning the elastane fibre are reproduced in Table 1.

Table 1:

Tabular overview of spinning conditions:

	Temperatures [°C]		Speed [m/min]		
Example number	**Chimney**	**Spinning gas**	**Godet 1**	**Godet 1**	**Take-up unit**
1	250	350	670	780	800
2	250	350	670	780	800
3	250	350	670	780	800
4	250	350	670	780	800
5	250	350	670	780	800
C1	230	270	670	780	800
C2	210	250	370	410	420

Winder from IWKA, type S200 VE

Chimney length: 5.3 m; gas throughput 30 m^2/h

The filaments thus obtained were examined and characterized with regard to their mechanical and thermal properties. This involved measuring in particular the tenacities and the ultimate tensile stress extensions (UTSE) on the lines of DIN 53834 Part 1. To this end, tensile tests were carried out on the elastane filament yarns in the conditioned state. For this, the prepared specimen is placed in a loop around the hook of the measuring head and around a 10 mm wrapping clamp using a pretensioning force of 0.001 cN/dtex. The total clamped length is 200 mm. A small piece of aluminium foil is attached as a marker at exactly the level of a light barrier. The carriage moves at an extension rate of 400%/min (800 mm take-off) to break the yarn and returns to its original position after measurement. 20 measurements are carried out per sample. In addition, a thermomechanical analyzer (TMA) was used to determine the heat distortion temperature (HDT). This involves determining the lengthening characteristics of a slightly pretensioned (0.2 mg/dtex) elastomer yarn (100 mm) while the temperature is raised continuously at 20°C/min. Above a certain temperature (HDT), the yarn undergoes lengthening without any further increase in the temperature. The HDT is determined by placing 45° tangents against the corresponding curves. The higher the resulting HDT, the greater the corresponding interactions of the hard segments. Table 2 shows the filament properties determined.

Table 2:

Tabular comparison of yarn data:

Example number	Linear density dtex	Tenacity cN/dtex	UTSE %	HDT °C
1	44.9	1.01	432	183
2	44.5	0.99	428	185
3	47.0	1.01	579	169
4	47.2	0.91	435	184
5	46.8	0.96	424	181
C1	45.9	0.81	516	187
C2*	49.6	1.18	461	171

UTSE: ultimate tensile strength extension; HDT: heat distortion temperature

Fibre obtained at a take-up speed of 800 m/min

*Fibre obtained at take-up speed of 420 m/min.

The dry spinning process produced multifilaments having an average linear density of 45 dtex. It is observed that especially the use of polyethers having comparatively high molecular weights (M=2900) provides very good mechanical filament properties which in some instances are even superior to those of the standard systems (consisting of 4,4'-methylenediphenyl diisocyanate and polyethers having molecular weights of M=2000) produced under identical conditions (C1). The thermal data of these standard systems are achieved in particular through the use of polyethers having molecular weights of M=2000. The above-described processes then provide a simple way of synthesizing, on the basis of all aliphatic building blocks, polyurethaneurea elastanes which, compared with conventional systems, have similar or in some instances even superior filament properties.

In addition, the fibre materials obtained were investigated with regard to their fastness to light and atmospheric contaminants (especially NO_x) and with regard to their whiteness. The tests were carried out in accordance with ISO 105-B02 (light fastness), ISO 105-G01 (NO_x fastness) and Datacolor 3890 with regard to the whiteness. To this end, the fibre materials were processed into a knitted sock and subjected to the respective fastness tests and whiteness investigations either as untreated raw material or after an acidic or alkaline bleach. Table 3 details the composition of the bleaching recipes:

Table 3:

Bleaching recipes for elastane fibre samples

	oxidative/ alkaline	reductive/ acidic	Fibre adds	
			oxidative/alkaline	reductive/acidic
Diadavin NSE 200%	0.5 ml/l		20% of elastane:	
H_2O_2 (35% strength)	6.0 ml/l		30 g	
Waterglass	2.0 ml/l			
$MgSO_4$	0.2 g/l		80% of cotton:	
Blankophor BA liq.	1.0%		120 g	
NaOH	pH 11			
Diadavin NSE 200%		0.5 ml/l		20% of elastane:
Blankit CP		3.0 g/l		30 g
Blankophor CA 42067		1.8%		80% of polyamide:
Acetic acid/sodium acetate		pH 5		120 g

Procedure: mix at RT, raise to 90°C over 30 min, hold at 90°C for 1 h, cool down, rinse, air-dry

Tables 4 and 5 supply the fastnesses and whiteness levels of the treated elastane materials.

Table 4:

Tabular comparison of light and NO_x fastnesses:

Sample No.	Raw material			After oxidative/alkaline bleach			After reductive/acidic bleach		
	Light	1xNO_x	3xNO_x	Light	1xNO_x	3xNO_x	Light	1xNO_x	3xNO_x
1a	5	3	2-3	5-6	2-3	2-3	5	3	2-3
1b	5-6	2-3	2-3	5-6	3-4	3	5	4-5	3-4
5a	5-6	3	2-3	5-6	2-3	1-2	5-6	2-3	2
5b	5-6	2-3	2	5	2-3	2	4	3	2-3
C1	3	2-3	2	2-3	2	1	2	1-2	1
C2	5	3	2-3	4	2	1-2	4	1-2	1

1a and 5a without stabilizer; 1b, 5b, C1 and C2 with 1% by weight of Cyanox 1790 as stabilizer (based on total solids)

What is reported is the rating of a visual assessment of colour against a scale going from 1 (poor) to 6 (very good).

Table 5:

Tabular comparison of Datacolor 3890 Berger whiteness data:

Sample No.	Raw material			After oxidative/alkaline bleach			After reductive/acidic bleach		
	un-treated	Light	3xNO$_x$	un-treated	Light	3xNO$_x$	un-treated	Light	3xNO$_x$
1a	82.1	56.4	60.8	67.2	54.2	48.4	95.3	67.8	70.6
1b	74.2	56.7	54.9	62.3	50.4	49.2	86.9	62.2	78.4
5a	85.0	74.3	62.3	72.8	54.2	40.9	114.9	101.6	85.4
5b	74.8	60.6	44.9	68.6	42.1	43.7	111.5	72.3	85.6
C1	83.4	63.7	58.0	81.3	43.9	38.5	86.5	45.6	-17.6
C2	62.7	17.3	29.1	59.2	0.7	4.6	77.7	1.9	16.1

1a and 5a without stabilizer; 1b, 5b, C1 and C2 with 1% by weight of Cyanox 1790 as stabilizer (based on total solids)

It is clear that the all aliphatic materials prepared and tested according to the invention are appreciably more stable with regard to their fastnesses after treatment with light or NO_x gas and also with regard to their whiteness than comparative systems based on aromatic diisocyanates. These effects are especially clear from a comparison of the data in Tables 4 and 5 after performance of bleaching treatments especially the reductive/acidic bleach. Elastane materials prepared according to the invention provide similar values in the light and atmospheric contaminants tests regardless of the respective pretreatments (bleach). It is particularly interesting to note that these excellent stabilities of these filament materials produced according to the present invention can be obtained even without addition of a stabilizer substance such as, for example, Cyanox 1790.

It is accordingly noted that elastane materials prepared according to the present invention on the basis of all aliphatic building blocks have not only good to very good yarn properties but also elevated resistance to pollutant gases and light compared with conventional, aromatic elastane systems, fully achieving the object of the invention of providing such materials.



Claims

1. Multistage process for preparing polyurethaneureas by preparing a prepolymer in solution or in the melt and then chain-extending the prepolymer in solution or in the melt, which comprises a first step of preparing the prepolymer (which is also referred to as "isocyanate-capped glycol") from

A) a polymeric diol of the general structure HO-Q-OH,
where Q is

a radical: $-[(CH_2)_nO]_m-$ or $-[(CH_2)_pCH(CH_3)CH_2O]_o-$
wherein n is a number from 2-10, m is a number from 1-150, o is a number from 1-150 and p is a number from 0-2,

a polyester radical prepared on the basis of adipic, sebacic, succinic or dodecanedioic acid or mixtures of these acids with diols of the general structure

HO-A-OH,

where A is a radical: $-[(CH_2)_r(CR^1R^2)_qCH_2)_s]-$,
wherein r is a number from 1-5, q is a number from 0-1,
s is a number from 0 to 5
and R^1 and R^2 are independently -H or $-CH_3$,
it being possible to use not only mixtures of these diols but also a single diol,

a polycaprolactone radical, preferably having a molecular weight of 500 to 5000,

or a polycarbonate radical such as a poly(pentane-1,5-carbonate) or poly(hexane-1,6-carbonate) radical, preferably having a molecular weight of 500 to 5000,

or a mixture of such polymeric diols A), and also

* C L M S *

B) an aliphatic or cycloaliphatic, especially cycloaliphatic, diisocyanate such as 1,6-hexane diisocyanate (HDI), 1,4-butane diisocyanate (BDI), 1,4-cyclohexyl diisocyanate (CDI), 4,4'-dicyclohexylmethane diisocyanate ($H_{12}MDI$), isophorone diisocyanate (IPDI), tetramethylxylylene diisocyanate (TMXDI) or dimeryl diisocyanate (DDI) or mixtures of these diisocyanates

having an NCO:OH ratio of 1.3 to 3.0, preferably of 1.5 to 2.3
either in a solvent such as dimethylformamide (DMF), dimethylacetamide (DMAc) or N-methylpyrrolidine (NMP) or some other dipolar aprotic solvent
or in the melt,
by heating the components, after they have been mixed, to 30°C to 100°C, preferably 40°C to 80°C, in the case of the use of solvents, or to 60°C to 200°C, preferably 80°C to 150°C, in the case of a reaction in the melt, for a duration of 0.5 to 5 hours, preferably 1 to 5 hours, with stirring,

a subsequent second step at a temperature of 0°C to 100°C of mixing further diisocyanate B) into the reaction mixture so that the total ratio of NCO:OH is 1.7 to 6.0,

and a third step of reacting the chain extension
either in the presence of a solvent such as dimethylformamide (DMF), dimethylacetamide (DMAc) or N-methylpyrrolidine (NMP) or other dipolar aprotic solvents both batchwise with stirring and continuously with careful mixing at a temperature of -20°C to 100°C, preferably 0°C to 80°C
or in the melt at a temperature of 100°C to 250°C using

C) an aliphatic or cycloaliphatic, especially cycloaliphatic, diamine selected from the group consisting of ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, 1,4-diaminobutane, 1,5-diaminopentane, 1,3-diaminocyclohexane, diaminomethyl-cyclohexane, isophoronediamine or mixtures of such diamines and triamines such as diethylenetriamine and optionally using

D) a primary or secondary, aliphatic and/or cycloaliphatic amine such as diethylamine, ethanolamine, di-n-butylamine or cyclohexylamine, especially diethylamine, ethanolamine, di-n-butylamine,

the molar ratio of diamine to amine based on amino groups being 100:0 to 100:20, preferably to 100:10, using a molar amine excess based on reactive isocyanate units of 0 to 25%, preferably 0 to 15%.

2. Process according to Claim 1, characterized in that the polymeric diol

A) has the general structure HO-Q-OH,
where Q is
a radical: $-[(CH_2)_nO]_m-$
wherein n is 4, m is a number from 10-70.

3. Process according to Claim 1 or 2, characterized in that the polymeric diol A) has the general structure HO-Q-OH,

where Q is a polyester radical prepared on the basis of adipic, sebacic, succinic or dodecanedioic acid with diols of the general structure:

HO-A-OH

where A is a radical: $-[(CH_2)_r(CR^1R^2)_q(CH_2)_s]-$,
wherein r is a number from 1-5, q is a number from 0-1, s is a number from 0 to 5
and R^1 and R^2 are independently -H or $-CH_3$.

4. Process according to any of Claims 1-3, characterized in that the aliphatic or cycloaliphatic diisocyanate B) is 1,4-butane diisocyanate (BDI), 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI), isophorone diisocyanate (IPDI) or a mixture thereof.

5. Process according to Claims 1-4, characterized in that the mixing and reacting of the further diisocyanate B) with the reaction mixture in the second stage is

effected at a temperature of 20°C to 80°C, so that the total ratio of NCO:OH is 1.7 to 5.0.

6. Process according to Claims 1-5, characterized in that the chain extension in the third stage is carried out in such a way that the molar ratio of isocyanate structures to Zerevitinov-active hydrogen atoms of the amines is 1.25:1 to 1:1.25.

7. Process for preparing elastane fibre, filament or yarn (hereinafter simplified to elastane yarn) by spinning a polyurethaneurea solution by the dry spinning process, characterized in that a spinning solution comprising a polyurethaneurea obtainable according to any of Claims 1 to 6 is spun through a spinnerette into a chimney, the solvent is removed at a chimney temperature of 150°C to 350°C, preferably 180°C to 250°C, and a spinning gas temperature of 150°C to 380°C, preferably 220°C to 360°C, the solidified yarn is taken off, optionally drawn, optionally set, spin finished and wound up on bobbins.

8. Process for preparing elastane fibre, filament or yarn by spinning a polyurethaneurea solution by the wet spinning process into a coagulation bath with fibre formation through coagulation, removing the solvent in the coagulation bath, washing the yarn product, preferably in water, drying the yarn, optionally drawing, optionally setting, spin finishing and winding up on bobbins, characterized in that the spinning solution used comprises a polyurethaneurea obtainable from the process according to any of Claims 1 to 6.

9. Melt spinning process for preparing elastane fibre by preparing a polyurethaneurea melt by the prepolymer process and spinning the polymer melt obtained, characterized in that the polyurethaneurea melt is prepared by the process according to any of Claims 1 to 6, the polymer melt is spun directly following its preparation, and the resulting elastane fibre is cooled, optionally drawn, spin finished and wound up.

10. Process for preparing elastane fibre according to Claim 9, wherein the polymer melt obtained following chain extension is initially cooled and

granulated instead of being directly spun and the resulting polymer granules are melted and melt spun into elastane yarn.

11. Polyurethaneureas based on

A) a polymeric diol of the general structure HO-Q-OH,
where Q is
a radical: $-[(CH_2)_nO]_m-$ or $-[(CH_2)_pCH(CH_3)CH_2O]_o-$
wherein n is a number from 2-10, m is a number from 1-150,
o is a number from 1-150 and p is a number from 0-2,

a polyester radical prepared on the basis of adipic, sebacic, succinic and/or dodecanedioic acid with diols of the general structure

HO-A-OH,

where A is a radical: $-[(CH_2)_r(CR^1R^2)_qCH_2)_s]-$,
wherein r is a number from 1-5, q is a number from 0-1,
s is a number from 0 to 5
and R^1 and R^2 are independently -H or $-CH_3$,

it being possible to use not only mixtures of these diols but also a single diol,

a polycaprolactone radical

or a polycarbonate radical such as poly(pentane-1,5-carbonate) diol or poly(hexane-1,6-carbonate) diol

or a mixture of such polymeric diols A), and also

B) isophorone diisocyanate (IPDI)

C) an aliphatic or cycloaliphatic diamine selected from the group consisting of

ethylenediamine, 1,2-propylenediamine, 1,3-propylenediamine, 1,4-diaminobutane, 1,5-diaminopentane, 1,3-diaminocyclohexane, diaminomethylcyclohexane, isophoronediamine or mixtures of such diamines and triamines such as diethylenetriamine and optionally using

D) a primary or secondary, aliphatic and/or cycloaliphatic amine such as diethylamine, ethanolamine, di-n-butylamine or cyclohexylamine.

12. Elastane yarn obtainable from a process according to any of Claims 7 to 10.

13. Use of the elastane yarn according to Claim 12 for preparing yarn especially combination yarn with other synthetic and nonsynthetic yarn fibre or filament and for preparing textile fabrics, such as consecutive course formation knits, wovens or simultaneous course formation knits.