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LINEAR SEGMENTED POLYURETHANES

Wilhelm Thoma, Berg. Neukirchen, Harald Oertel, Odenthal-Globusch, and Heinrich Rinke, Leverkusen, Germany, assignors to Farbenfabriken Bayer Aktiengesellschaft, Leverkusen, Germany

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ABSTRACT OF THE DISCLOSURE

Linear segmented polyurethanes containing chain extending segments derived from monoureadihydrazides and a process for their production. The polyurethanes are useful in the production of elastomeric filaments.

This invention relates to highly elastic linear segmented polyurethanes comprising segments which result from the use of monoureadihydrazides as chain extenders, and to a process for their production.

It is known that substantially linear, relatively high molecular weight, NCO preadducts (NCO preadducts or NCO prepolymers in short), obtained from relatively high molecular weight polyhydroxy compounds (optionally together with relatively small quantities of low molecular weight diols) and a molar excess of organic diisocyanates, can be reacted, in highly polar organic solvents such as dimethyl formamide, with substantially bifunctional chain extenders containing two active hydrogen atoms, resulting in the formation of viscous solutions of substantially linear polyurethane elastomers, which can be converted from the solution into elastic filaments or films.

Diamines, preferably aliphatic or araliphatic diamines, hydrazine or dihydrazide compounds in particular, are used as chain extenders. Diamines and hydrazine show a high level of reactivity to NCO preadducts which preferably contain aromatically bound NCO groups, with the result that there is a considerable danger of non-homogeneous crosslinked components ("jellyfish") being formed in the elastomer solution. A number of chemical modifications, or expensive technical apparatus, are required to reduce this tendency towards crosslinking.

By contrast, when dihydrazide compounds are used as chain extenders (cf. German patent specification 1,123,467) their level of reactivity to NCO preadducts is so low that their reaction can be displaced particularly effectively without any signs of undesirable chemical crosslinking or of "jellyfish" being formed in the solution. Polyurethane elastomer solutions of this kind can be spun into highly elastic filaments of high tensile strength and limited permanent elongation. It has been found, however, that elastomeric filaments of this kind under an initial tension, stretch to a far greater extent in hot air than in air at room temperature and, following relaxation, show a high residual elongation. Residual elongation remains high even after hydrothermal treatment (for example in boiling water) of, in particular elastomeric, filaments under an initial tension (for example at 100% elongation). This limited resistance to elongation under thermal or hydrothermal conditions of dihydrazide-extended elastomeric filaments, extended for example with succinic acid or adipic acid dihydrazide, is particularly undesirable in finishing and dyeing processes.

In addition, elastomeric filaments of this kind react, for example when carbodihydrazide is used as chain extender and under the effect of traces of certain metal ions (for example Cu^{++} or Mg^{++}), in such a way that the filaments discolour, thus detrimentally affecting the appearance of undyed fabric, even though there may be no evidence of any effect upon their strength properties.

If bis-semicarbazides, for example 1,2-ethylene bis-semicarbazide or 1,4-tetramethylene-bis-semicarbazide, are used instead of dihydrazides for the reaction with the NCO preadducts, the solubility of these bis-semicarbazides is highly unfavourable so that, depending upon the structure of the bis-semicarbazides, they remain partly undissolved even in boiling dimethyl formamide. In addition, it is impossble to obtain elastomer solutions which can be spun on an industrial scale, because they are converted into a gel-like state as early as during preparation or after a short time. In all probability, the polyurethane elastomers formed are inadequately solvated by the solvent with the result that they are precipitated in the form of a pasty gel, which is either impossible or extremely difficult to convert into filaments or films. It is only possible by addition of relatively large quantities of salts, such as $LiCl_2$, $CaCl_2$ or $CaBr_2$, to obtain solutions from them at elevated temperatures. Unfortunately, the addition of salts such as these has a deletrious effect upon the spinning properties of the solutions.

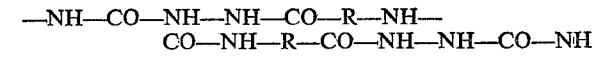
Alkylene-bis-carbazine esters have also been proposed as chain extending agents for polyurethanes. Unfortunately, polyurethanes chain-extended with alkylene-bis-carbazine esters have relatively low melting points, and filaments spun from polyurethanes chain extended in this way show extremely unsatisfactory thermal and hydrothermal behaviour, that is to say, they are elongated to considerable extent at elevated temperatures, and especially when tested in hot water, and following relaxation show extremely high residual elongations.

In addition, there is a considerable decrease in tension in hot water when filaments or fabrics are kept at certain elongations. In many instances, the filaments actually break when tested in hot water. This behaviour of elastomeric filaments is of considerable disadvantage when fabrics made from them are treated under tension either in hot water or in steam, in finishing and dyeing processes (cf. comparison tests in the examples).

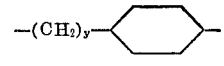
It is an object of this invention to provide new linear segmented polyurethanes with improved properties. It is another object of this invention to provide a process for the production of these new linear segmented polyurethanes that avoids the disadvantages in the hitherto known processes by the use of new chain extending agents.

Other objects will be evident from the following description and the examples.

These objects are accomplished by a linear segmented polyurethane comprising chain extending segments, at least 5 mol percent of which consists of a chain-extension segment of the structure



in which R represents a radical of the formula $-(CH_2)_x-$ (wherein x represents 1 or 2) or of the formula



(wherein y represents 0, 1 or 2).

These linear segmental polyurethanes are a process which comprises reacting an isocyanate preadduct, with an NCO-group content of from 1.0 to 6.0% by weight with a substantially equivalent quantity of a bifunctional low molecular weight consisting of at least 5 mol percent,

based in the total of chain-extending agent, of a monourea dihydrazide of the formula

$$H_2N—NH—CO—R—NH—CO—NH—R—CO—NH—NH_2$$

in which R represents an alkylene radical with 1 or 2 carbon atoms or an aromatic or araliphatic radical of the formula



(wherein y represents 0, 1 or 2), said reaction being carried out and up to 95 mol percent of a chain extending agent selected from the group consisting of water, a glycol and a compound of the formula $H_2N—Z—NH_2$, wherein Z is a single bond or a bivalent organic radical, in the presence of a highly polar organic solvent, and then removing the solvent.

The removing of the solvents in this process can be effected by evaporation or coagulation, preferable by a wet spinning process.

This procedure thus gives a linear segmented polyurethane elastomer comprising a reaction product of a relatively high molecular weight diisocyanate with a chain-extending agent, containing chain-extending segments of the structure

$$—NHCO—NH—NH—CO—R—NH—CO—NH—R—CO—NH—NH—CO—NH—$$

In addition to the monourea dihydrazides, other bifunctional chain extenders can be used; preferably at least 55 mol percent of the chain extenders required for the chain-extending reaction with the NCO preadduct are constituted by the monourea dihydrazides, although at least 5 mol percent of the chain-extending agents should be monourea dihydrazides. Accordingly, the corresponding elastomers contain at least 5 mol percent and preferably at least 55 mole percent, based on the total amount of chain-extending segments present, of segments with the structure

$$—NH—CO—NH—NH—CO—R—NH—CO—NH—R—CO—NH—NH—CO—NH—$$

In view of the properties of elastomers containing dihydrazides, for example carbodihydrazide, or succinic or adipic acid hydrazide, as chain-extenders, it was extremely surprising that monourea dihydrazides corresponding to the formula

$$H_2N—NH—CO—R—NH—CO—NH—R—CO—NH—NH_2$$

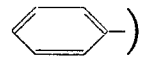
give elastomers with outstanding properties, considerably better than those of comparable elastomers extended with dihydrazides. The solubility of the monourea dihydrazides in highly polar solvents is also sufficient for carrying out a normal chain-extending reaction. Polyurethane elastomers extended with urea diacetic acid hydrazide and urea dipropionic acid hydrazide [R represents $—CH_2$ or $(CH_2)_2—$] show particularly outstanding properties, so that they are preferably used as bifunctional compounds containing two active hydrogen atoms, for chain-extending the NCO preadducts, particularly when the polyurethanes are to be converted into elastomeric filaments. After spinning from solution by conventional dry-or-wet-spinning processes, elastomers of this kind give high grade elastomeric filaments with considerably improved thermal and hydrothermal properties, coupled with outstanding strength and elastic properties. The filaments and films are colourstable to heavy metals, for example, copper ions, and show a better resistance to hydrolysis than comparable dihydrazide compounds. In addition, the polyurethane elastomers are readily soluble in the usual solvents, for example dimethyl formamide or dimethyl acetamide, dimethyl sulphoxide or N-methyl pyrrolidone.

With the exception of urea diacetic acid hydrazide (K. Schlogl, Monatsh. 83 (1952), 507), the monourea dihydrazides used as chain extenders in accordance with the invention are all new compounds. These new compounds include urea-N,N'-dipropionic acid hydrazide, urea-N,N'-diphenyl-4,4'-carboxylic acid hydrazide, urea-N,N'-diphenyl-4,4'-diacetic acid hydrazide, and urea-N,N'-diphenyl-4,4'-dipropionic acid hydrazide. Even limited structural modification, for example the use of urea di-(methyl acetic acid)-hydrazide, urea di-butyric acid hydrazide or urea diphenyl-3,3'-carboxylic acid hydrazide is sufficient to reduce the thermal and hydrotherminal properties of the elastomeric filaments made from elastomers chain-extended with these hydrazides to an inadequate level.

The novel compounds can be obtained, for example, by the hydrazinolysis of alkyl or aryl esters (methyl, ethyl or phenyl ester being preferred) of the corresponding urea dicarboxylic acids:

$$R'—OCO—R—NH—CO—NH—R—COOR' + 2H_2N—NH_2 \cdot H_2O \rightarrow H_2N—NH—CO—R—NH—CO—NH—R—CO—NH—NH_2 + 2R'—OH$$

(wherein R' represents CH_3, C_2H_5, or



The urea dicarboxylic acids and dicarboxylic acid esters are obtained from amino acids and amino acid esters respectively by the action of phosgene or diphenyl carbonate.

To synthesise the elastomers, a substantially linear, relatively high molecular weight, NCO preadduct obtained from a relatively high molecular weight polyhydroxy compound (optionally together with a relatively small quantity of a low molecular weight dihydroxy compound) and excess of a diisocyanate, are reacted in a highly polar organic solvent with a substantially equivalent quantity of a chain-extender (a monourea dihydrazide, optionally in admixture with known chain-extenders).

The following processes are examples of the principal methods of preparing elastomers containing the

$$(—NH—CO—NH—NH—CO—R—NH)_2\ CO\text{-segment}$$

which is formed through the reaction of

$$H_2N—NH—CO—R—NH—CO—NH—R—CO—NH—NH_2$$

and the NCO groups of (relatively high molecular weight) diisocyanates:

(a) The reaction of the NCO preadduct of a relatively high molecular weight dihydroxy compound and a molar excess of a diisocyanate (NCO content of the preadduct approximately 1% to 6% NCO, based on the solids content), with a substantially equivalent quantity of a bifunctional low molecular weight chain-extending agent containing two active hydrogen atoms in the presence of highly polar organic solvents, wherein the chain extending agent is a monourea dihydrazide of the formula

$$H_2N—NH—CO—R—NH—CO—NH—R—CO—NH—NH_2$$

(the radical R is as defined above).

(b) Reaction as in (a), except that in addition to at least 5 mol percent and preferably more than 55 mol percent of the monourea dihydrazide used according to the invention, up to 95 mol percent and preferably up to 45 mol percent, of a conventional bifunctional compound with two active hydrogen atoms and a molecular weight of from 18 to about 300 (for example water, hydrazine, or an amino alcohol, diamine, dihydrazide, semicarbazide hydrazide, semicarbazide carbazine ester, or semicarbazide amine) is also used as chain-extender.

(c) Reacting an isocyanate preadduct containing approximately 1 to 6% of NCO, obtained from a relatively high molecular weight dihydroxy compound, a low

molecular weight diol preferably with one or two tertiary amino groups in the molecule and with molecular weight of from 62 to about 300, in a quantity of from about 0.05 to 1.0 mol per mol of relatively high molecular weight dihydroxy compound, and a molar excess of a diisocyanate with a substantially equivalent quantity of a monourea dihydrazide of the formula

$$H_2N—NH—CO—R—NH—CO—NH—R—CO—NH—NH_2$$

as chain extender, in a highly polar solvent.

(d) Reacting an isocyanate preadduct prepared as described in method (c) with a substantially equivalent quantity of a chain extender, at least 5 mol percent and preferably more than 55 mol percent of a monourea dihydrazide of the formula

$$H_2N—NH—CO—R—NH—CO—NH—R—CO—NH—NH_2$$

and up to 95 mol percent and preferably up to 45 mol percent of a conventional chain extender being used.

The products obtained by the process are linear segmented polyurethane elastomers consisting of characteristic intralinear segments with the ideal structure I

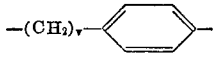
$$[—(O—D—O—CO—NH—Y—NH—CO—)_r(—O—G—O—CO—NH—Y—NH—CO)_s]_m—[—NH—NH—CO—R—NH—CO—NH—R—CO—NH—NH—CO—NH—Y—NH—CO—]_n$$

in which D represents a long-chain bivalent, substantially aliphatic polymer radical derived by loss of terminal hydroxy groups from a relatively high molecular weight polyhydroxy compound with a melting point below 60° C. and a molecular weight of from 500 to 6000, without any substituents that are reactive to isocyanate,

Y represents a bivalent organic radical derived from an aromatic, aliphatic, cycloaliphatic or araliphatic diisocyanate,

G represents a divalent aliphatic, cycloaliphatic or araliphatic radical derived by loss of terminal hydroxy groups from a dialcohol with a molecular weight of from 62 to 300, preferably containing one or more tertiary aliphatic amino groups.

R represents a bivalent organic radical, for example $—(CH_2)_x—$ (where x=1 or 2) or



(where v=0, 1 or 2)

r is an integer of at least 1, for example from 1 to 5, preferably from 1 to 3,

s=0 or an integer of at least 1, for example from 1 to 5, preferably 1,

m=1 or an integer, for example from 1 to 5, preferably from 1 to 3, and

n=1 to 5, preferably 1 or 2.

The elastomers have a breaking elongation of more than 300% and an intrinsic viscosity (measured on a 1% by weight solution in hexamethyl phosphoramide at 25° C.) of at least 0.5, to give adequate elastic properties in the filaments and films.

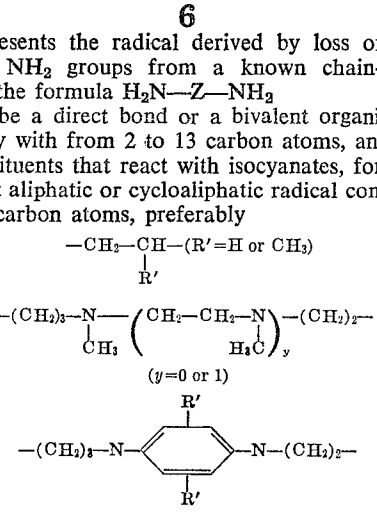
In addition to structural segments of Formula I, the substantially linear segmented polyurethane elastomers may contain up to a maximum of 95 mol percent, and preferably up to 45 mol percent, of intralinear segments obtained by reacting the NCO preadducts with known chain-extenders such as water, amino alcohols or compounds containing two terminal NH_2 groups, and may have the structure II

$$—[—(O—D—O—CO—NH—Y—NH—CO—)_r—(O—G—O—CO—NH—Y—NH—CO)_s—]_m—[NH—Z—NH—CO)_n—NH—Y—NH—CO—]_p$$

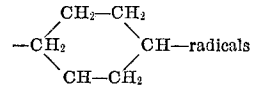
in which D, G, Y, r, s, m and n are as defined above, p=0 or 1 and

Z represents the radical derived by loss of the two terminal NH_2 groups from a known chain-extending agent of the formula $H_2N—Z—NH_2$

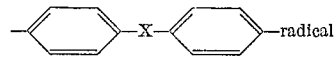
Z can be a direct bond or a bivalent organic radical, preferably with from 2 to 13 carbon atoms, and without any substituents that react with isocyanates, for example a divalent aliphatic or cycloaliphatic radical containing at most 13 carbon atoms, preferably



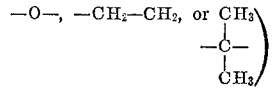
cis/trans mixture of



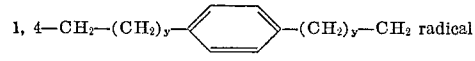
a divalent aromatic radical, without any condensed rings, preferably a



(wherein X is a direct bond or



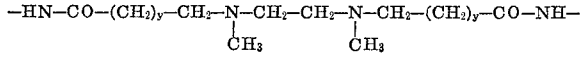
a bivalent araliphatic radical, preferably a 1,3- or



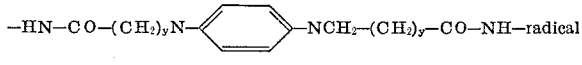
(y=0 or 1); or a radical

$$—HN—CO—R''—CO—NH—$$
$$—HN—CO—NH—R''—NH—CO—NH—$$

where R'' represents a divalent organic radical with up to 13 carbon atoms, preferably an aliphatic, cycloaliphatic or aromatic radical, preferably an



or



or the radical $—HN—CO—(CH_2)_2—NH—CO—NH—$

Examples of suitable relatively high molecular weight, substantially linear, polyhydroxyl compounds containing terminal hydroxyl groups (HO—D—OH) include polyesters, polyester-amides, polyethers, polyacetals, polycarbonates or poly-N-alkyl urethanes, the above compounds optionally containing other groups, such as ester, ether, amide, urethane or N-alkyl urethane groups, with molecular weights of from 600 to 6000, and preferably from 800 to 3000, and melting points preferably lower than 60° C., and with even greater advantage lower than 45° C. It is also possible to use mixtures of the relatively high molecular weight polyhydroxyl compounds.

The following compounds are particularly suitable: polyesters of adipic and optionally mixtures of dialcohols, for example ethylene glycol, propylene glycol, 1,4-butane diol, 2,5-hexane diol, 2,2-dimethyl-1,3-propane diol, 1,6-hexane diol, 2,2-dimethyl-1,3-propane diol, 1,6-hexane diol, 2-methyl-1,6-hexane diol, 2,2-dimethyl-1,3-hexane diol p-bis-(hydroxymethyl) cyclohexane, 3-methyl-1,4-pentane diol, and 2,2-diethyl-1,3-propane diol, preferably those with diols or mixtures of diols containing 5 or more

carbon atoms because polyesters of this kind show a relatively high resistance to hydrolysis and, especially when diols containing lateral alkyl radicals are also used, the end products show high elasticity at low temperatures. Polyesters obtained by the polyaddition of caprolactone with glycols in a narrow molecular weight distribution are also suitable starting materials.

Polyurethane elastomers with an outstanding resistance to hydrolysis can be obtained from polyalkylene ethers, for example polytrimethylene ether diols or polypropylene glycols, and preferably from polytetramethylene ether diols, which may also be used as mixed polyethers (through the incorporation by condensation of small quantities of epoxides, such as propylene oxide or epichlorohydrin) or following end-group modification, for example replacing the OH groups by the

O—CO—N—(alkyl)—CH_2—CH_2—CH

group. Polyepichlorohydrins with terminal OH groups in the aforementioned molecular weight range are also suitable for flameproof end products. Basic polyethers, whose tertiary amino groups may be quaternised (optionally in part), are also suitable.

Suitable polycarbonates include those containing 1,6-hexane diol as the sole or predominant dialcohol in addition to other diols, or those of -hydroxy caproic acid-'-hydroxyhexyl ester.

Aliphatic, cycloaliphatic, araliphatic, aromatic, diisocyanates and heterocyclic diisocyanates, optionally in admixture with one another, may be used as diisocyanates (C=O=N—Y—N=C=O). Aromatic diisocyanates of symmetrical structure are particularly suitable, for example diphenyl methane-4,4'-diisocyanate, diphenyl, dimethylmethane-4,4'-diisocyanate, phenylene-1,4-diisocyanate, 2,2', 6,6'-tetramethyl diphenyl methane-4,4'-diisocyanate, diphenyl - 4,4' - diisocyanate diphenyl ether-4,4' - diisocyanate, or their alkyl-, alkoxyl- or halogen-substituted derivatives, tolylene-2,4- and 2,6-diisocyanates and their commercial mixtures, 2,4-diisopropyl phenylene - 1,3 - diisocyanate, m-xylylene diisocyanate, p-xylylene diisocyanate and a,a,a',a' - tetramethyl - p - xylylene diisocyanate, also alkyl- or halogen substitution products of the aforementioned diisocyanates, for example 2,5-dichloro-p-xylylene diisocyanate or tetrachloro - p-phenylene diisocyanate, dimeric tolylene-2,4-diisocyanate or bis-(3-methyl-4-isocyanatophenyl)-urea. Aliphatic or cycloaliphatic diisocyanates such as hexane-1,6-diisocyanate, cyclohexane-1,4-diisocyanate, dicyclohexyl methane-4,4'-diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl cyclohexane or 2,2,4-trimethyl hexane-1,6-diisocyanate may be used, optionally in portions, and give products which show little or no discolouration under the effect of light. Diisocyanates such as, '-di-(isocyanatoethyl)-benzene or 1,2,3,4,5,6-hexahydrodiphenylmethane-4,4'-diisocyanate also give products which show little discoloration under the effect of light.

By virtue of the fact that they are easy to obtain on a commercial scale, it is preferred to use diphenyl methane-4,4'-diisocyanate, diphenyl ether-4,4'-diisocyanate, p-phenylene, diisocyanate, isomeric tolylene diisocyanate and (optionally in portions) hexane-1,6-diisocyanate and the cis/cis- and/or cis/trans- and/or trans/trans-isomers of dicyclohexyl methane-4,4'-diisocyanate.

To prepare the substantially linear, relatively high molecular weight, isocyanate preadducts, the relatively high molecular weight polyhydroxyl compounds HO—D—OH described above are reacted with the diisocyanates in molar excess, for example in a molar ratio of from 1:1.25 to 1:4.0, and preferably in a molar ratio of from 1:1.30 to 1:2.5, the diisocyanates optionally being added in stages either in the melt or in solvents such as tetrahydrofuran, dioxan, ethyl acetate, 2-butanone, chlorobenzene or dimethyl formamide at temperatures of up to about 130° C. and preferably at temperatures in a range from 70 to 100° C. Reaction temperatures of from 20 to 70° C. are preferred when dimethyl formamide is used as the reaction medium. When the relatively high molecular weight hydroxyl compounds have molecular weights at the lower end of the stated range, for example from 650 to 1250, the diisocyanates are preferably reacted with low molar ratios, for example from about 1:1.25 to 1:2.0; and in higher molar ratios, for example of from 1:1.5 to 1:2.5; where the relatively high molecular weight hydroxyl compounds have molecular weights higher in the stated range, for example from 1500 to 2500.

When a polyhydroxy compound HO—D—OH is reacted with a diisocyanate OCN—Y·NCO in a molar ratio of 1:2, an NCO preadduct with the ideal structure

OCN—Y—NH—CO—O—D—CO—NH—Y—NCO

is formed. If the reaction is carried out in a molar ratio of 1:1.5 (=2:3), an NCO preadduct of the general structure

OCN—Y—NH—CO—O—D—O—CO—NH—Y—NH
—CO—O—D—O—CO—NH—Y—NCO

is formed. A product of the same structure is obtained when the polyhydroxy compounds are reacted with an OH/NCO ratio of 2:1 and the novel "pre-extended" dihydroxy compound is subsequently converted, optionally with another diisocyanate, into the isocyanate preadduct in a CN/NCO ratio of 1:2. Statistical mixtures of corresponding NCO preadducts are formed when using other molar ratios.

To prepare the isocyanate preadducts, it is possible to use relatively small quantities of low molecular weight diosl HO—G—OH with molecular weights of 62 to about 300, particularly those containing one or more tertiary amino groups, in addition to the relatively high molecular weight polyhydroxyl compounds HO—D—CH during the reaction with the diisocyanates. The diols may be added in admixture with the relatively high molecular weight polyhydroxy compounds, or at any time during or even after the NCO preadduct formation from diisocyanate and relatively high molecular weight polyhydroxy compounds. Examples of these diols include ethylene glycol, butane-1,4-diol, bis-N,N-(β - hydroxyethyl) - methylamine, bis-N,N-(β-hydroxyethyl) - ethylene diamine, N,N-dimethyl-N,N' - bis - (β - hydroxypropyl)-ethylene diamine, N,N'-bis - (β - hydroxypropyl)-piperazine, N.N'-bis-(β-hydroxyethyl) - piperazine and hydroquinone - bis - (β - hydroxyethyl ether). The use of diols containing tertiary amino groups above all increases affinity for dyes, improves light stability and provides the starting point for further after-treatments, for example crosslinking reactions with 4,4'-bis-chloromethyl diphenyl ether.

The low molecular weight diols are generally used in a quantity of from 0.05 to 1.0 mol, and preferably in a quantity of from 0.05 to 0.5 mol, and with particular advantage in a quantity of from 0.07 to 0.25 mol, per mol of polyhydroxy compound in the formation of the NCO preadducts. The quantity of diisocyanate used is best increased beyond the molar ratios which have just been specified by a quantity corresponding to that of the low molecular weight diol, for example from 0.05 to 1.0 mol. This results in the formation of isocyanate preadducts of the structure:

OCN—Y—NH—CO—C—D—O—CO—NH—Y—NH
—CO—O—G—O—CO—NH—Y—NCO—

or, in the case of "pre-extension" for example, in the formation of an NCO preadduct of the structure:

OCN—Y—NH—CO—O—D—O—CO—NH—Y—NH
—CO—O—D—O—CO—NH—Y—NH—CO—O—G
—O—CO—NH—Y—NCO

The typical structural segments of the isocyanate preadducts (which may also be referred to as "relatively high molecular weight diisocyanates"), resulting from pre-extension" or from glycol incorporation, are formed in a more or less statistical sequence and may optionally occur

repeatedly. The NCO-group content of the isocyanate preadduct (expressed as percent by weight of NCO in the solvent-free NCO preadduct) is of a decisive importance to the properties of the polyurethane elastomers obtained from them. Generally, the reaction with the monourea dihydrazides used as chain-extenders in accordance with the invention can only be carried out with NCO preadducts whose NCO content in the solids component is at least 1.0%; the isocyanate preadducts should preferably have an NCO content of from 1.5 to about 6% by weight. Isocyanate contents of from 1.75 to 3.5%, based on the solids content of the isocyanate preadduct, are particularly preferred when the elastomers obtained from them are to be used for the production of elastomeric filaments.

Monourea dihydrazides of the formula

$$H_2N—NH—CO—R—NH—CO—NH—R—CO—NH—NH_2$$

are used as bifunctional chain-extending agents containing two active hydrogen atoms in substantially equivalent quantities. based on the NCO groups in the NCO preadduct, preferably as sole chain-extenders but also as component chain-extenders. Urea diacetic acid hydrozide and urea dipropionic acid hydrazide are particularly preferred.

In addition to at least 5 mol percent, and preferably more than 55 mol percent, of the monourea dihydrazides, however, it is also possible to use up to 95 mol percent, and preferably up to 45 mol percent, of other commercial chain-extenders with molecular weights of from 18 to about 300, such as water, glycols, and diamine compounds corresponding to the formula $H_2N—Z—NH_2$ in which Z is as defined above.

Suitable conventional chain-extenders include for example water, aminoalcohols such as aminoethanol, and organic compounds containing two terminal NH_2 groups, for example hydrazine (or hydrazine hydrate); aliphatic or cycloaliphatic diamines, preferably ethylene diamine, 1,2-propylene diamine, cis- and/or trans-1,3-diamino cyclohexane, N,N-bis-(Y-aminopropyl)-methylamine, N,N'-dimethyl - N,N,' - bis - (Y - aminopropyl) - ethylene diamine, N,N'-bis (Y-aminopropyl)-piperazine, or N,N'-bis - (Y - aminopropyl-2,5-dimethyl piperazine; aromatic diamines, preferably, 4,4'-diamino diphenyl methane, 4,4'-diamino diphenyl ether, 4,4'-diamino diphenyl ethane, or 4,4'-diamino diphenyl dimethyl methane; araliphatic diamines such as m or p-xylylene diamine, 1,4-bis-(β-aminoethyl)- benzene or a,a,a',a'-tetramethyl - p - xylylene diamine; or dihydrazides, bis-semicarbazides or bis-carbazine ester such as carbodihydrazide, terephthalic acid dihyrazide, hydroquinone diacetic acid dihydrazide, aminoethanol, 1-amino-3-propanol, aminoacetic acid hydrazide, methylamino-N,N-bis-(propionic acid hydrazide), piperazine-N,N'-bis-(propionic acid hydrazide) or N,N'-dimethyl ethylene diamine - N,N' - bis - (propionic acid hydrazide).

The chain-extension reactions may also be carried out stepwise or with mixtures of the chain-extending agents.

To reduce the molecular weight and to obtain polyurethane elastomers which are still soluble, despite any molecular branching that may have occurred, it is also possible to use monofunctional compounds, for example butylamine, dibutylamine, acetic acid hydrazide, butyl semicarbazide, N,N-dimethyl hydrazine, or 1-butanol, in small quantities, for example from 0.01 to 10 mol percent, based on the NCO content (for chain-terminating reactions).

Reaction of the isocyanate preadducts with the chain-extending agent is preferably carried out with equivalent quantities (based on the NCO content), for example from 100 to 120 mol percent and preferably from 100 to 110 mol percent, of chain-extending agents, preferably at temperatures of from about 0 to 130° C., advantageously from 20 to 80° C., in solvents.

The higher the excess of chain-extenders, the lower will be the molecular weight of the polyurethane, due to chain termination. It is possible to adjust the required molecular weight and the required solution viscosity (according to German patent specification No. 1,157,386) by the careful addition of other, preferably less reactive, aliphatic diisocyanates or triisocyanates. After the required viscosity has been reached, carboxylic acid anhydrides, for example acetic anhydride, phthalic anhydride or other substances with an acylating effect, for example acid chlorides or carbamic acid chlorides, may be used to stabilise the as yet unreacted terminal groups by reaction with monoisocyanates, for example butyl isocyanate.

Suitable solvents include highly polar organic water soluble solvents, preferably with boiling points from about 140 to 225° C., which contain amide, urea or sulphoxide groups and which are capable of forming strong hydrogen bridge bonds, for example dimethyl formamide, diethyl formamide, formamide, dimethyl acetamide, formyl morpholine, hexamethyl phosphoramide, tetramethyl urea, dimethyl sulphoxide, dimethyl cyanamide or mixtures thereof. Commercially preferred solvents include dimethyl formamide or dimethyl acetamide. Less polar solvents, which on their own are not able to dissolve polyurethanes and polyurethane ureas, for example tetrahydrofuran, dioxan, acetone, ethylene glycol monomethyl ether acetate or chlorobenzene, can be added to the highly polar solvents in minor quantities, amounting for example to 33% by weight of the total amount of solvent. The concentration of the elastomer solutions should be from about 5 to 43% by weight, and preferably from about 10 to 33% by weight, the viscosities lying in the range from 1 to 1000 poises and preferably from about 50 to 800 poises at 20°. The molecular weight of the segmented elastomers according to the invention should be so high that the intrinsic viscosity

$$\eta_i = \frac{\ln \eta_R}{C}$$

measured at 25° C. should be at least 0.5, and preferably from 0.70 to 0.9, when 1.0 g. of elastomer is kept dissolved in 100 ml. of hexamethyl phosphoramide solution (phosphoric acid tri-dimethyl amide) at 20° C. In the above equation, η_R represents the relative viscosity (ratio of the throughflow time of the solution to the throughflow time of the solvent), whilst C represents the concentration in g./100 ml. The melting points of the elastomers determined on a Kofler bench, should be above 200° C. and preferably above 230° C., when the elastomers are to be used as starting materials for elastomeric filaments.

The solutions of the polyurethanes and polyurethane ureas can be mixed with organic or inorganic pigments, dyes, optical brighteners, UV absorbers, phenolic antioxidants, in particular light stabilizers such as N,N-dialkyl semicarbazides or N,N-dialkyl hydrazides, and substances with a crosslinking effect for example paraformaldehyde, melamine hexamethylol ether or other formaldehyde derivatives, such as dimethylol dihydroxy ethylene urea, dimethylol ethylene urea, trimethylol melamine or dimethylol urea dimethyl ether, quarternising agents, for example dichloromethyl durene, or polyaziridine ureas, for example hexamethylene-ω, ω-bis-ethylene imide urea. Resistance to the dissolving and swelling effect of highly polar solvents can be modified, for example, by a thermally-initiated cross-linking reaction.

The solvent can be removed from the elastomer solutions by a variety of methods known per se, including evaporation or coagulation, optionally accompanied by formation of the required shaped articles, such as filaments or films. Films or coating can be obtained by drying the elastomer solution on substrates, for example glass plates or textile materials. Filaments can be obtained by wet or dry spinning. Microporous coatings can be formed by brush coating elastomer solutions on to (optionally textile) substrates (for example webs), optionally in the presence of moist air, followed by coagulation in non-solvents for the polyurethane, for example water or aque-

ous solutions. The microporosity of the films can be increased even further by suitable additives, such as finely divided salts, emulsifiers or soluble polyamides.

In the following examples, temperatures are given in ° C.

The films or filaments referred to in the examples were prepared and investigated by the following standard processes:

Films: obtained by brush-coating the elastomer solution on to glass plates followed by drying (for 30 minutes at 70° C. and 45 minutes at 100° C.), ultimate thickness approximately 0.15 to 0.25 mm. In some instances, filaments with a thickness of from about 250 to 800 dtex, were cut from the films by means of a film-slicing or cutting machine and then tested.

Wet-spinning: a preferably 20% by weight elastomer solution is spun at a rate of approximately 1 ml. per minute through a nozzle with 20 bores, each 0.12 mm. in diameter, into a coagulation bath heated to a temperature from 80 to 85° of 90% by weight of water and 10% by weight of dimethyl formamide (length approximately 3 metres), and after passing through the washing zone (water at 90° C.) the filaments obtained are wound up at a take-off rate of 5 metres per minute. The bobbins are kept in hot water (50° C.) for 1 hour and then dried.

Dry-spinning: a preferably 24 to 25% by weight elastomer solution is spun through a nozzle with 16 bores, each 0.20 mm. in diameter, into a 5 metres long shaft heated to a temperature from 220° to 250° C. into which is blown air heated to a temperature from 210 to 280° C. The filaments are taken off at a rate of approximately 100 metres per minute and, following preparation with a talcum suspension, are wound up for example at a rate of from 125 to 175 metres per minute, optionally with stretching. The filaments can then be subjected to an after-treatment, either on bobbins or in a continuous cycle. (The spinning rates may be even higher, for example from 300 to 400 metres per minute.)

Breaking elongation is measured in a tensile testing machine in which the length of the filament between grips is controlled by a photocell, and the degree of slip through the grips is compensated.

The modulus 300% (in the first elongation curve), the modulus 150% (in the 3rd return curve) and the permanent elongation (after 3×300% elongation, 30 seconds after relaxation) are determined in order to characteristise the elastic properties.

Determination of the heat distortion temperature (HDT) of elastomeric filaments:

The denier of elastomeric filaments laid out for 3 hours in the absence of tension under normal climatic conditions is determined (by weighing a length of filament under an initial tension or load of 0.045 mg./dtex). An elastomeric filament with a length between the grips of 250 mm. is suspended at room temperature in a tube containing air filled with nitrogen under an initial tension of 1.8 mm./dtex.

The tube is surrounded by a heating jacket through which a silicone oil heated by way of a thermostat flows. The temperature prevailing in the tube is initially increased to around 125° C. over a period of some 30 minutes. A further increase in temperature is carried out at a rate of 3° C. every 5 minutes until the elastomeric filament has undergone a change in length to more than 400 mm. The measurements obtained are recorded in a graph in such a way that, on the abscissa, 1 unit of length corresponds to a temperature difference of 20° C., whilst on the ordinate axis, one unit corresponds to a change in length of the elastomeric filament of 20 mm. The heat distortion temperature is that temperature which is read off from the abscissa by vertically projecting the point of contact of the 45° tangent to the temperature/length change curve.

The temperature stability of the elastomers is generally assessed as being greater, the higher the HDT value. The value should be at least 140° C., and should be at least 145° C., and preferably higher than 150° C., for high grade elastomeric filaments.

Determination of the decrease in tension of elastomeric filaments in hot water (HWSA):

A length of filament length between grips 100 mm., initial load 0.9 mg./dtex) is elongated or extended by 100% at 20° C. and the tension prevailing after 2 minutes (mg./dtex) is measured (first value). The filament, still stretched by 100%, is then immersed in water at 95° C. and the tension prevailing after a residence time of 3 minutes is measured (second value). After this measurement has been taken, the filament is removed from the water bath and left standing for 2 minutes at room temperature. The pre-extended filament, which is still between the grips, is relaxed until free from tension, and the residual elongation is immediately determined (3rd value). Scheme of reproduction in the examples (abbreviation HWSA):

Tension values		Residual elongation after relaxation, 3d value
1st value	2d value	
In air at 20° C. (mg./dtex).	In water at 95° C. (mg./dtex).	(In air) at 20° C., percent.

The hydrothermal properties are assessed as being higher, the greater the second value (tension in hot water) in mg./dtex and the smaller the third value (residual elongation after treatment in the relaxed state). The tension value in water should be at least 13.5 mg./dtex, a level of at least 18 mg./dtex being required of high grade elastomeric filaments. Following hydrothermal treatment, residual elongation in the relaxed state should be less than 45% and preferably, less than 40%.

Determination of the elongation of elastomeric filaments in hot water (HWL):

A weight of 27 mg./dtex is attached, by means of a clip or grip, to a 50 mm. long piece of filament, and left hanging for 25 minutes in air at room temperature. After 25 minutes, percentage elongation is roughly determined (1st value). The filament thus extended, together with the weight by which it is tensioned, is immediately immersed in water at 95° C. and the elongation which it undergoes in water is read off after 25 minutes. The result is expressed as a percentage elongation, based on the length between the grips of 50 mm. (2nd value). The weighted filament is then removed from the hot water bath, after which permanent residual elongation is measured by removing the weight until the filament is free from tension (3rd value).

Scheme of reproduction in the examples (abbreviation HWL):

Elongation		Residual elongation, 3d value
1st value	2d value	
In air at 20° C., percent.	In water at 95° C., percent.	After relaxation in air at 20° C., percent.

The hydrothermal properties are assessed to be higher the smaller the second value (elongation in hot water) and the smaller the third value (permanent elongation after relaxation).

In the case of high grade elastomeric filaments, the second value should be less than 250% and preferably less than 150%. Residual elongation (3rd value) should be less than 150% and preferably less than 100%.

The melting point of the elastomeric substance is measured on a film strip after a residence time of 2 minutes on a Kofler bench, and for elastomeric filaments should be above 200° C. and preferably above 230° C.

PREPARATION OF THE UREA-N,N'-DICARBOXYLIC ACID HYDRAZIDES

(a) Urea-N,N'-dipropionic acid hydrazide

$$H_2N—NH—CO—(CH_2)_2—NH—CO—NH—(CH_2)_2—CO—NH—NH_2$$

M.P. 199° C., M.W. 232.25.

178 g. of urea dipropionic acid ethyl ester are dissolved in 450 ml. of alcohol. 144 g. of hydrazine hydrate are added dropwise to the boiling solution, after which the reaction mixture is kept boiling for 1 hour. After cooling (ice-sodium chloride), the crude dihydrazide is obtained in a yield of 95.5%. It is recrystallised from 3 ml./g. of alcohol+1.4 ml./g. of water; M.P. 199° C.,

$C_7H_{16}N_6O_3$ (232.25).—Calculated (percent): O, 20.67. Found (percent): O, 20.7.

UREA DIPROPIONIC ACID ETHYL ESTER

153.5 g. of β-alanine ethyl ester hydrochloride are suspended in 200 ml. of benzene. 56.0 g. of potassium hydroxide in 150 ml. of water are added at 5 to 10° C. to liberate the ester.

A phosgene solution is prepared by dissolving 50 g. of phosgene in 450 ml. of benzene. Half the solution is added dropwise over a period of 1 hour at 5 to 10° C. to the two-phase alanine ester solution. A solution of 29.5 g. of potash and 25 g. of potassium bicarbonate in 150 ml. of water is then run in, followed by the dropwise addition of the second half of the phosgene solution over a period of 1 hour. This is followed by stirring for 1.5 hours at 20° C. Some of the urea ester is precipitated between the phases. Following separation of the aqueous phase, the benzene is distilled off in vacuo from a glass beaker equipped with a stirring mechanism. The crude urea ester accumulates in the form of a white crystal mass, crude yield 123 g. or 94.5%, M.P. 92° C.

12.5 ml. of water are added to 112 g. of β-isocyanato propionic acid ethyl ester (A. Goldschmidt and M. Wick, Ann. 575 (1952) 217) dissolved in 100 ml. of acetone. After 4 days, the urea dipropionic acid ethyl ester is filtered under suction. Yield 90%, M.P. 94° C.

38.3 g. of β-alanine ethyl ester hydrochloride are dissolved in 80 ml. of alcohol. A sodium ethoxide solution of 5.75 g. of sodium in 125 ml. of alcohol is added at 0 to 5° C. 36 g. of β-isocyanatopropionic acid ethyl ester in 50 ml. of acetone are added dropwise to the alcoholic solution of the β-alanine ester containing suspended sodium chloride. On completion of the reaction, the acetone and some of the alcohol are distilled off in vacuo, the reatcion mixture is poured on to 500 ml. of water and the urea dipropionic acid ethyl ester is filtered under suction. Yield 71%, M.P. 96° C.

$C_{11}H_{20}N_2O_5$ (260.3).—Calculated (percent): N, 10.76. Found (percent): N, 10.4.

β-alanine ethyl ester hydrochloride (Lengfeld und Stieglitz Am. Chem. J. 15, 510).

Esterification of the β-alanine with alcohol/HCl proceeds very readily. Since according to literature references, the ester hydrochloride is almost impossible to isolate on a large scale by the addition of ether to the esterification solution while cooling, the following procedure is adopted:

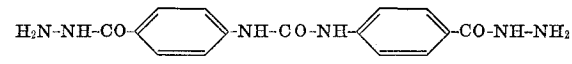
712 g. of β-alanine (8.0 mols) are suspended in 920 ml. of alcohol and 400 g. of HCl gas are introduced into the resulting suspension. The mixture is brought to the boil over a period of 20 minutes and kept boiling for a total of 120 minutes. A clear solution is obtained after 90 minutes. On completion of esterification, 460 ml. of benzene are added and the water of esterification formed is azeotropically distilled off. Finally, the residual benzene and the alcohol are distilled off in vacuo (bath temperature up to 110° C.). The β-alanine ethyl ester hydrochloride is obtained in a quantitative yield in the form of an oil which crystallises after standing.

UREA-N,N'-DIPROPIONIC ACID METHYL ESTER

200 g. of β-alanine are suspended in 260 ml. of methanol. 85 g. of HCl gas are introduced while stirring, beginning at room temperature and followed by quick heating to boiling point. The β-alanine is dissolved during esterification. The reaction is over after 3 hours. The solution of the β-alanine methyl ester hydrochloride cooled to 0° C. is diluted with 100 ml. of methanol, followed by the addition of 126 g. of caustic potash in 400 ml. of methanol at 0° C. in order to liberate the amino acid ester. Following the addition of 160 g. diphenyl carbonate, the reaction mixture is brought to the boil over a period of 15 minutes. The methanol is then distilled off and the residue is stirred with 1.3 litres of methylene chloride. In order to separate the phenol eliminated, the methylene chloride solution is washed twice with 8% by weight sodium hydroxide solution and twice with water. The urea dimethyl ester is isolated from the methylene chloride solution in a yield of 75%, and can be recrystallised from 2 ml./g. of ethyl acetate, M.P. 103–104° C.

$C_9H_{16}N_2O_5$ (232.2).—Calculated (percent): N, 12.06; O, 34.45. Found (percent): N, 12.1; O, 34.1.

(b) Urea-N,N'-diphenyl-4,4'-dicarboxylic acid hydrazide



M.P. 248° C., M.W. 328.35.

50 g. of hydrazine hydrate are introduced into 100 ml. of pyridine at 80° C. 77.0 g. of urea-N,N'-diphenyl carboxylic acid phenyl ester dissolved in 400 ml. of pyridine are then added. The reaction mixture is heated for 1 hour at 80° C., and cooled; the resulting white deposit is suction-filtered and the crude urea-N,N'-diphenyl carboxylic acid hydrazide is washed thoroughly with alcohol. Yield 88%, M.P. 248° C.

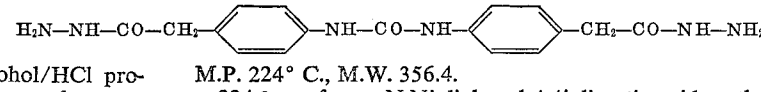
UREA-N,N'-DIPHENYL-4,4'-DICARBOXYLIC ACID PHENYL ESTER

106.5 g. of 4-aminobenzoic acid phenyl ester are dissolved in 300 ml. of pyridine. A solution of 35 g. of phosgene in 200 ml. of toluene is then added dropwise at 15° C. and the reaction mixture is subsequently heated for 30 minutes at 40° C. After cooling, the reaction solution is stirred into ice water, and the deposit is washed thoroughly with water and dried. Yield: 75%, M.P. 252° C. The substance can be dissolved in and reprecipitated from 2 ml./g. of DMF by the addition of 3 ml./g. of water.

$C_{27}H_{20}N_2O_5$ (452.5).—Calculated (percent): O, 17.68. Found (percent): O, 17.9.

$C_{15}H_{16}N_6O_3$ (328.35).—Calculated (percent): N, 25.60. Found (percent): N, 25.7.

(c) Urea-N,N'-diphenyl-4,4'-diacetic acid hydrazide



M.P. 224° C., M.W. 356.4.

224.0 g. of urea-N,N'-diphenyl-4,4'-diacetic acid methyl ester are heated at boiling point over a period of 5 hours with 140 g. of hydrazine hydrate in 750 ml. of dioxan. The precipitate which is actually formed during the reaction is suction-filtered while cooling. Yield 92%, M.P. 224° C.

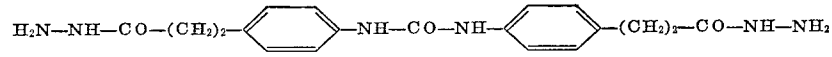
$C_{17}H_{20}N_6O_3$ (356.4).—Calc. (percent): C, 57.29; H, 5.66; N, 23.58. Found (percent): C, 57.9; H, 5.7; N, 23.4.

UREA-N,N'-DIPHENYL-4,4'-DIACETIC ACID METHYL ESTER

145 g. of phosgene are introduced at 10 to 15° C. into a solution of 366 g. of 4-aminophenyl acetic acid methyl ester in 300 ml. of acetone to which 114 g. of caustic soda in 600 ml. of water are simultaneously added. The reaction mixture is then stirred for 1 hour and poured on to ice water, and the urea ester precipitated is suction-filtered and washed thoroughly with water. Yield 86%, M.P. 217° C.

$C_{19}H_{20}N_2O_5$ (356.4).—Calc. (percent): C, 64.03; H, 5.66; O, 22.45. Found (percent): C, 63.8; H, 6.0; O, 22.7.

(d) Urea-N,N'-diphenyl-4,4'-dipropionic acid hydrazide



M.P. 270–273° C., M.W. 384.

85.0 g. of urea diphenyl-4,4'-dipropionic acid methyl ester are dissolved under heat in 200 ml. of pyridine, and the resulting solution is run, with heating, into a hot solution of 105 g. of hydrazine hydrate in 50 ml. of pyridine. Signs of precipitatte formation are noticed soon after the urea ester has been added. The mixture is kept boiling for 1.5 hours and cooled, and the dihydrazide is suction-filtered, suspended in alcohol, suction-filtered and dried. Yield 82.5%, M.P. 270–273° C.

$C_{19}H_{24}N_6O_3$ (384.5).—Calculated (percent): N, 21.86. Found (percent): N, 21.2.

UREA-N,N'-DIPHENYL 4,4'-DIPROPIONIC ACID METHYL ESTER

140 g. of 4-aminophenyl-propionic acid methyl ester are introduced into 150 ml. acetone. 55 g. of phosgene are introduced into the acetone solution over a period of 30 minutes at 10 to 15° C., and 40.5 g. of NaOH in 225 ml. of water are simultaneously added dropwise. The mixture is stirred without cooling for a period of 1 hour, during which nitrogen is passed through the reaction mixture, after which everything is poured into 1 litre of ice water. The crude urea ester is recrystallised from 2 ml./g. of alcohol+1 ml./g. of dimethyl formamide. Yield 84%, M.P. 188–191° C.

$C_{21}H_{24}N_2O_5$ (384.4).—Calculated (percent): N, 7.29. Found (percent): N, 7.2.

PREPARATION OF THE POLYURETHANE ELASTOMERS

Example 1

100 g. of a mixed polyester of adipic acid and a glycol mixture of 1,6-hexane diol/2,2-dimethyl-1,3-propane diol in a molar ratio of 65:35 (OH number 66.0) and 2.0 g. of N,N'-bis-(β-hydroxypropyl)-methylamine are heated for 60 minutes at 110° C. with 4,4'-diphenyl methane diisocyanate. The melt is dissolved in 100 g. of chlorobenzene. The NCO content amounts to 1.40% by weight (corresponding to 2.49% by weight in the solids component).

7.15 g. of urea-N,N'-diacetic acid hydrazide are dissolved at 120° C. in 370 g. of DMF. 200 g. of the NCO prepolymer solution are stirred into the solution of the chain-extender heated to 80° C. The viscosity of the elastomer solution is further increased by the addition of 2.0 ml. of a 10% by weight solution of hexane-1,6-diisocyanate in dioxan. The viscous 20.9% by weight elastomer solution is pigmented with 4% by weight of titanium dioxide, based on the solids content of the elastomer, and cast into films from which filaments are cut and then wet-spun into fibres (cf. general procedure). The properties of the filaments are set out in Table 1 and compared with the results from comparison tests, especially with succinic acid dihydrazide as chain-extender. After one hour in a solution of copper sulphate in amomnia ($n/20$ $CuSO_4$), the elastomeric filaments do not show any signs of discolouration, and have a melting point of from 230 to 235° C. (Kofler bench).

Example 2

100 g. of the polyester described in Example 1 (molecular weight 1650) are dehydrated following the addition of 0.1 ml. of a 33% by weight SO_2 solution of dioxan. Following the addition of 2.1 g. of N-ethyl-bis-(β-hydroxypropyl) amine, the polyhydroxy compounds are heated for 60 minutes at 100° C. with 28.6 g. of 4,4'-diphenyl methane diisocyanate. The NCO prepolymer melt is then dissolved in 100 g. of dioxan giving a solution with an NCO content of 1.39% by weight (calculated 1.43% by weight). 8.15 g. of urea-N,N'-dipropionic acid hydrazide are dissolved in 35 ml. of water (20° C.), and 320 g. of dimethyl formamide (50° C.) are added to this solution. 200 g. of NCO prepolymer solution are run into the clear aqueous solution with thorough stirring. The viscous elastomer solution formed is pigmented with 18.5 g. of a 33.3% by weight TiO_2 paste (1 part by weight of rutile, 1 part by weight of dimethyl formamide and 1 part by weight of elastomer solution), i.e. 4% by weight of TiO_2 based on elastomer substance. The solution (27.4% by weight) is cast into films and, after dilution to a concentration of 20% by weight, is wet-spun into filaments.

The properties of the filaments are set out in Table 1 and compared with the results of comparison tests, especially with results obtained when using adipic acid hydrazide. The elastomeric filaments do not show any signs of discolouring when stored in an ammoniacal N/20 $CuSO_4$ solution, and have a melting point of from 232 to 235° C.

Example 3

200 g. of the polyester described in Example 1 are dehydrated following the addition of 0.2 ml. of a 30% by weight SO_2 solution in dioxan. Following the addition of 4.0 g. of N-methyl-bis-(β-hydroxypropyl)-amine in 10 g. of chlorobenzene, the hydroxy compounds are heated for 90 minutes at 100° C. with 53.8 g. 4,4'-diphenyl methane diisocyanate. The melt is dissolved in 190 g. of chlorobenzene, the solution has an NCO content of 1.09% by weight (corresponding to 1.94% by weight in the solids component). 8.80 g. of urea-N,N'-diphenyl-4,4'-carboxylic acid hydrazile are dissolved at 120° C. in 100 g. of N-methyl-pyrrolidone. This solution of the chain-extending agent is diluted with 220 g. of dimethyl formamide heated to 70° C. 200 g. of the NCO prepolymer solution are stirred at 70° C. into the extender solution. The 23.1% by weight viscous elastomer solution formed is pigmented with 4% by weight of TiO_2, based on solid elastomer. The elastomer solution is cast into films from which cut filaments are prepared. The properties of the filaments are set out in Table 1. The filaments have a melting point of 238 to 242° C. (Kofler bench).

Example 4

100 g. of the polyester described in Example 1 are dehydrated as described in Example 3. Together with 2.0 g. of N-methyl-bis-(β-hydroxypropyl)-amine, the polymer is heated for 90 minutes at 100° C. with 29.2 g. of 4,4'-diphenyl methane diisocyanate. The NCO prepolymer melt is dissolved in 100 g. of chlorobenzene. The solution has an NCO content of 1.42% by weight (corresponding to 2.50% by weight in the solids component).

12.50 g. of urea - N,N' - diphenyl-4,4'-diacetic acid hydrazide are dissolved at 70° C. in 300 g. of DMF. 200 g. of the NCO prepolymer solution are stirred at 50° C. into the solution of the chain-extending agent. The highly viscous elastomer solution is cast into films from which cut filaments are prepared and wet-spun into filaments. The properties of the filaments are set out in Table 1. The filaments have melting point of from 235 to 238° C. (Kofler bench).

Example 5

100 g. of the polyester described in Example 1 are dehydrated as in Example 3. Following the addition of 2.0 g. of N-methyl-bis-(β-hydroxypropyl)-amine, the polyester is heated for 90 minutes at 100° C. with 26.9 g. of 4,4'-diphenyl methane diisocyanate. The NCO prepolymer melt is taken up in 100 g. of chlorobenzene, the NCO content amounts to 1.10% by weight (corresponding to 1.96% by weight in the solids component).

10.60 g. of urea-N,N'-diphenyl-4,4'-propionic acid hydrazide are dissolved at 180° C. in 200 g. of N-methyl

pyrrolidone. This solution is diluted with 120 g. of dimethyl formamide heated to 100° C. 200 g. of the NCO prepolymer solution are stirred in at 95° C. After pigmenting with rutile (4% by weight), the 23.1% by weight highly viscous elastomer solution is cast into films, from which cut filaments are prepared. The properties of the filaments are set out in Table 1. The filaments have a melting point of from 236 to 238° C. (Kofler bench).

Example 6

100 g. of a linear polyhydroxy carbonate of ω-hydroxyphenyl-ω'-hydroxycaproic acid ester and diphenyl carbonate with an OH number of 65.0 are heated for 60 minutes at 100° C. with 24.0 g. of 4,4'-diphenyl methane diisocyanate. The NCO prepolymer melt is dissolved in 200 g. of methyl ethyl ketone giving a solution with an NCO content of 1.05% by weight (corresponding to 2.73% by weight in the solids component).

8.00 g. of urea-N,N'-dipropionic acid hydrazide and 0.65 g. of 4,4'-diamino diphenyl methane are dissolved at 140° C. in 250 g. of DMF. 300 g. of the NCO prepolymer solution are stirred into the solution of the two chain-extending agents at 50° C. The viscous 22.0% by weight elastomer solution has a viscosity of 100 poises at 20° C. The solution is wet-spun into filaments and, in addition to films, cut filaments are prepared from the films, M.P. 243° C. (Kofler bench). The properties of the filaments are set out in Table 1.

Example 7

1000 g. of a polytetramethylene ether diol with an OH number of 109.5 are reacted for 20 minutes at 70 to 72° C. with 216 g. of N,N'-bis-(β-hydroxypropyl)-methylamine. 402.8 g. of diphenyl methane-4,4'-diisocyanate and 160 g. of dioxan, and the reaction mixture is quickly cooled to room temperature. The prepolymer solution has an NCO content of 2.72% by weight. 27.1 g. of finely ground urea-N,N'-dipropionic acid hydrazide are suspended at 90 to 95° C. in 991 g. of dimethyl formamide, 364 g. of the above NCO prepolymer solution being introduced into the resulting suspension over a period of 3 minutes with thorough stirring. The suspended dihydrazide is dissolved during the reaction. A homogeneous elastomer solution with a viscosity of 390 poises at 20° C. is obtained, being pigmented with 4% by weight of titanium dioxide. Following the addition of 113 mg. of hexane diisocyanate, the viscosity of the spinning solution rises to 525 poises.

The elastomer solution is dry spun into a shaft heated to 220° C. and taken off at a rate of 100 metres per minute. Some of the filaments are wound on to bobbins without pre-elongation and others under a pre-elongation of 50%, and then thermofixed by heating on bobbins for 1 hour at 130° C. The properties are set out in Table 1.

The filament with a pre-elongation of $d=50\%$ was tested to determine its resistance to hydrolysis in a washing liquor of 5 g./litre of Marseilles soap and 2 g./litre of anhydrous soda at a washing temperature of 90° C. The following results which demonstrate the outstanding resistance to hydrolysis of the filaments were obtained:

		Tensile strength, g./dtex	Breaking elongation, percent	Modulus 300, mg./dtex
Original filament		0.83	485	247
Hydrolysis/90° C	4 hr.	0.87	502	306
	16 hr.	0.79	548	276
	32 hr.	0.75	530	258

Example 8

800 g. of a mixed polyester with the composition described in Example 1 (OH number 68) are reacted for 50 minutes at 95 to 98° C. with 15.4 g. of N,N'-bis-(β-hydroxypropyl)-methylamine, 144.7 g. of p-phenylene diisocyanate and 240 g. of chlorobenzene. After rapid cooling to room temperature, the NCO prepolymer has an NCO content of 2.03% by weight.

21.2 g. of urea-N,N'-dipropionic acid hydrazide are dissolved at 130° C. in 833 g. of dimethyl formamide, 358 g. of the NCO preadduct solution being added to the resulting solution in a matter of minutes at 90 to 97° C. A homogeneous elastomer solution with a viscosity of 246 poises is obtained. After pigmenting with 4% by weight of TiO_2, the viscosity is adjusted to 535 poises at 20° C. by the addition of 180 mg. of hexane-1,6-diisocyanate. Films are prepared from the elastomer solution by coating it on to glass plates and evaporating the solvent. After they have been cut into filaments by means of a film cutting machine, these films show the values set out in Table 1. The extremely high heat distortion temperature and the limited tendency of the filaments to discolour under light whilst retaining their strength, are remarkable in comparison with comparable tests based on diphenyl methane-4,4'-diisocyanate. The elastomer substance is found to have a melting point of 235° C. on a Kofler bench.

Example 9

18.0 g. of urea-N,N'-dipropionic acid hydrazide and 3.5 g. of piperazine-N,N'-dipropionic acid hydrazide are dissolved at 110–120° C. in 835 g. of dimethyl formamide, and reacted at 80° with 358 g. of the NCO preadduct solution from Example 8. After pigmenting with 4% by weight of TiO_2, a highly viscous noticeably light elastomer solution with a viscosity of 710 poises at 20° C. is obtained. The solution is converted into films, which are in turn converted into filaments which show the properties set out in Table 1. The filaments have a melting point of from 226 to 228° C. on a Kofler bench. The filaments are distinguished by a level of stability to light which is even more favourable than that in the preceding example.

Example 10

100 g. of a mixed polyester with the composition described in Example 1 (OH number 65.9) are heated for 170 minutes at 50° C. with 19.85 g. of N,N'-bis-(β-hydroxypropyl)-methylamine, 269.4 g. of diphenyl methane, 4,4'-diisocyanate and 322 g. of dimethyl formamide. After cooling to room temperature, the NCO prepolymer solution has an NCO content of 1.68% by weight.

10.29 g. of 2-semicarbazido-propionic acid hydrazide and 1.81 g. of urea-N,N'-dipropionic acid hydrozide are dissolved in 24 g. of water and diluted with 784 g. of dimethyl formamide. 374 g. of the above NCO prepolymer solution are stirred into this solution, resulting in the formation of a clear homogeneous colourless elastomer solution with a viscosity of 474 poises at 20° C. Following the addition of 92 mg. of hexane-1,6-diisocyanate, the viscosity rises to 540 poises. The solution is pigmented with 4% by weight of TiO_2 and is then wet- and dryspun. The properties of the filaments obtained are set out in Table 1.

Comparison tests.—300.0 g. of a mixed polyester of adipic acid and a glycol mixture of hexane-1,6-diol and 2,2-dimethyl-1,3-propane diol (molar ratio of the glycols 65:35), molecular weight 1690, are heated for 60 minutes at 100° C. with 6.0 g. of N,N'-bis-(β-hydroxypropyl)-methylamine, and 81.3 g. of diphenyl methane-4,4'-diisocyanate. The melt is taken up in 300.0 g. of dioxan and cooled to room temperature. The NCO preadducts solution has an NCO content of 1.27% by weight corresponding to 2.24% by weight of NCO in the solids component.

(A) Chain-extension with adipic acid dihydrazide.—5.52 g. of adipic acid dihydrazide are dissolved in 300 g. of DMF. 200 g. of the NCO preadduct solution are run in at 30° C., resulting in the formation of a clear homogeneous elastomer solution whose viscosity is 338 poises at 20° C. The solution is converted into filaments and films in the usual way. As can be seen from Table 2 (comparison tests), the elastomers extended with adipic acid dihy-

drazide, though showing good elastic properties, exhibit poor thermal properties (HDT) and totally unsatisfactory hydrothermal properties. The reaction according to the invention with urea-N,N'-dipropionic acid hydrazide gives elastomer (cf. Example 2) with considerably better thermal and hydrothermal properties than those extended with the structurally related adipic acid dihydrazide, which can be imagined as having been formed through omission of the urea group from the urea-N,N'-dipropionic acid hydrazide.

(B) Chain-extension with succinic acid dihydrazide.—4.65 g. of succinic acid dihydrazide are dissolved in 300 g. of DMF. As in comparision test (A) 200 g. of NCO prepolymer adduct solution are stirred in at 30° C. resulting in the formation of a clear highly viscous elastomer solution (610 poises at 20° C.) which is pigmented with 4% by weight of rutile, based on solid elastomer. The solution is converted into filaments and films in the usual way. As can be seen from Table 2, the elastomers extended with succinic acid hydrazide, though showing good elastic properties, exhibit totally unsatisfactory thermal and hydrothermal properties (compared in particular with Example 1).

(C) Chain-extension with carbodihydrazide.—2.85 g. of carbodihydrazide are dissolved in 300 g. of DMF. 300 g. of the NCO prepolymer solution are stirred in the solution of the carbodihydrazide heated to 70° C. A viscous clear elastomer solution is obtained with a viscosity rising to 645 P/20° C. following the addition of another 5.0 g. of the NCO preadduct solution. Filaments are formed in the usual way. The test results are set out in Table 2.

When treated with ammoniacal $CuSO_4$ solution, the filaments turn reddish brown in colour.

TABLE 1

Ex. No.	Filament according to process	Elastic Properties: Tensile strength	Breaking elongation (percent)	Modulus: 300%, mg./dtex	Modulus: 150% mg./dtex, 3d recovery curve	Perm. elong. after 3×300 (percent)	Thermal and hydrothermal properties: HDT, ° C.	HWSA: Tension in— Air 20°, mg./dtex	HWSA: Tension in— Water 95°, mg./dtex	HWSA: Residual elong. after hydrothermal loading (percent)	HWL: Elong. in— Air 20° (percent)	HWL: Elong. in— Water 95° (percent)	HWL: Residual elong. after relaxation (in air 20°) (percent)	Remarks: Behaviour in *n* 20 $CuSO_4$ solution (ammoniacal)
1	N	0.40	610	108	18	17	160	46.1	15.5	52	48	282		
	F	0.46	710	124	18	18								Colourless.
2	N	0.58	520	141	21	21	160	35.4	19.6	58	54	242	146	
	F	0.55	750	104	18	19								Colourless.
3	N						147							
	F	0.60	535	110	16	22								
4	N	0.44	400	180	17		154	30.6	15.7	65	30	240	144	
	F	0.43	530	108	15									Colourless.
5	N						159							
	F	0.65	550	103	16						76	310	188	Colourless.
6	N	0.54	445	127	18	24	169	40	17.1	48	60	232	118	
	F	0.59	555	116	16	20								Colourless.
7	T, V=0	0.61	620	141	19	20	178							
	T, V=50	0.83	485	247	22	20		55.8	22.6	44	38	132	60	Colourless.
	F	0.66	645	145	19	25								
8	T, V=0	0.45	690	60	12	29	190						100	Colourless.
	T, V=50	0.46	700	78	15	28								
	F	0.63	745	70	15	25								
9	T, V=0	0.45	720	51	11	30								
	T, V=50	0.46	700	70	13	27	180							Colourless.
	F	0.67	780	65	15	26								
10	N	0.56	460	151	21	13	161	38.9	16.8	31	66	286	100	
	F	0.53	560	99	18	10								Colourless.
	T, V=50	0.67	360	180	22	11		33.1	16.9	33	94	236	83	

NOTE.—Wet-spinning; F=filaments cut from film; T=dry-spinning; V=pre-elongated in percent.

TABLE 2

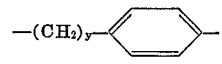
Ex. No.	Filament according to process	Elastic properties: Tensile strength	Elastic properties: Breaking elongation (percent)	Elastic properties: Modulus 300%, mg./dtex	Elastic properties: Modulus 150%, mg./dtex, 3d recovery curve	Elastic properties: Perm. elong. after 3×300 (percent)	Thermal and hydrothermal properties: HDT, ° C.	Thermal and hydrothermal properties: HWSA Tension in— Air 20°, mg./dtex	Thermal and hydrothermal properties: HWSA Tension in— Water 95°, mg./dtex	Thermal and hydrothermal properties: HWSA Residual elong. after hydrothermal loading (percent)	Thermal and hydrothermal properties: HWL elongation in— Air 20° (percent)	Thermal and hydrothermal properties: HWL elongation in— Water 95° (percent)	Thermal and hydrothermal properties: Residual elong. after relaxation (in air 20°) (percent)	Thermal and hydrothermal properties: Remarks: Behaviour in *n* 20 $CuSO_4$ solution (ammoniacal)
(A)	N	0.60	444	123	18	14	128	29.5	8.5	78	102	572	302	
	F	0.79	445	71	16	18								Colourless.
(B)	N	0.56	537	94	17	16	128	30.1	8.1	60	92	>800	Tear	
	F	0.64	623	79	17	13								Colourless.
(C)	N	0.68	542	101	19	16	145	32.2	10.4	50	44	354	142	
	F	0.68	547	96	19	13								Reddish-brown.

What we claim is:

1. A linear segmented polyurethane comprising chain-extending segments, at least 5 mol. percent of which consist of a chain-extension segment of the structure

—NH—CO—NH—NH—CO—R—NH—CO—
NH—R—CO—NH—NH—CO—NH—

in which R represents a radical of the formula $—(CH_2)_x—$ wherein *x* represents 1 or 2 or of the formula



wherein *y* represents 0, 1 or 2.

2. The linear segmented polyurethane of claim **1** wherein at least 55 mol. percent of said chain-extending segments have the structure

—NH—CO—NH—NH—CO—R—NH—CO—
NH—R—CO—NH—NH—CO—NH—

and up to 45 mol. percent of said chain-extending segments are derived from a chain-extending agent selected from the group consisting of water, a glycol and a compound of the formula $H_2N—Z—NH_2$, wherein Z is a single bond or a bivalent organic radical.

3. The linear segmented polyurethane elastomer of claim **1** having breaking elongation in excess of 300% and an intrinsic viscosity of at least 0.5 measured in a 1% by weight solution in hexamethylphosphoramide at 25° C., which comprises intralinear segments of the structure

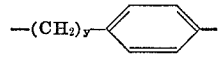
$$[—(O—D—O—CO—NH—Y—NH—CO)_r—$$
$$(O—G—O—CO—NH—Y—NH—CO)_s]_m—$$
$$[NH—NH—CO—R—NH—CO—NH—R—CO—$$
$$NH—NH—CO—NH—y—NH—CO]_n$$

in which

D is a long chain divalent aliphatic polymer radical derived from a relatively high molecular weight polyhydroxy compound with a molecular weight of from 600 to 5000 and a melting point below 60° C.,

Y represents a divalent organic radical derived from an aromatic, aliphatic, cycloaliphatic or araliphatic diisocyanate, G represents a divalent aliphatic, cycloaliphatic or araliphatic radical derived from a dialcohol with molecular weight of from 62 to 300 or of a dialcohol with molecular weight of from 62 to 300 containing 1 or more tertiary aliphatic amino groups,

R represents an alkylene radical with 1 or 2 carbon atoms or an aromatic or araliphatic radical of the formula



wherein *y* represents 0, 1 or 2

r is an integer of at least 1
s is 0 or an integer of at least 1
m is an integer of at least 1, and
n is an integer from 1 to 5.

4. The polyurethane of claim **3** wherein *r*, *s*, *m* and *n* each represent an integer from 1 to 5.

5. The polyurethane of claim 3 wherein r is an integer from 1 to 3, s is 1, m is an integer from 1 to 3, and n is 1 or 2.

6. A highly elastic polyurethane elastomer fiber comprising the linear segmented polyurethane of claim 1.

7. A polyurethane elastomer solution which comprises a solution of from 10 to 33% by weight of a polyurethane according to claim 1 and a polar aliphatic solvent containing an amide, urea or sulphoxide group and having a boiling point of up to 225° C.

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DONALD E. CZAJA, Primary Examiner

M. J. WELSH, Assistant Examiner

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