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POLYURETHANES CURED WITH AMINES
AND THEIR PREPARATION

ABSTRACT OF THE DISCLOSURE

Polyurethane prepolymers are described which are prepared from 2,4'-diisocyanate diphenylmethane (2,4'-MDI), a polyol component and an aliphatic diisocyanate. These prepolymers can be cured with aliphatic, cycloaliphatic and/or aromatic amines to form a cured urethane elastomer. In comparison to cured urethane elastomers based on monomeric 2,4'-MDI, these prepolymers provide elastomers with extended pour life, i.e. they exhibit a slower rate of viscosity buildup after curative and prepolymer are mixed which results in a reduced propensity to crack during the curing process and gives the opportunity to cast larger parts. In comparison to polyurea/urethanes prepared from cured TDI-prepolymers and which optionally include H12-MDI, the prepolymers of the invention have better health and safety aspects.

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Australian Patents Act 1990 – Regulation 3.2

**ORIGINAL COMPLETE SPECIFICATION
STANDARD PATENT**

Invention Title

Polyurethanes cured with amines and their preparation

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

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**POLYURETHANES CURED WITH AMINES
AND THEIR PREPARATION**

CROSS REFERENCE TO RELATED PATENT APPLICATION

- 5 The present patent application claims the right of priority of European Patent Application No. 07001845.2, filed 29 January 2007.

BACKGROUND OF THE INVENTION

- This invention relates to castable polyurethane and/or polyurethane/urea elastomer
10 compositions with improved processing characteristics, including longer pour life, reduced tendency to crack, as well as better health and safety aspects since they are free of toluene diisocyanate. Isocyanate-endcapped prepolymers are employed in the castable elastomers of the invention. Effective processes for the production of such prepolymers and elastomers are disclosed. These prepolymers can be substituted for TDI-prepolymers
15 and for aliphatic isocyanate based prepolymers with similar cure characteristics. The prepolymers of the invention, however, have improved health and safety aspects.

- Aromatic polyisocyanates are well known and are widely used in the preparation of polyurethane and polyurethane/urea elastomers. These aromatic diisocyanates generally include compositions such as 2,4-toluene diisocyanate (2,4-TDI), 2,6-toluene
20 diisocyanate (2,6-TDI), 4,4'-methylene-bis-(phenylisocyanate) and 2,4'-methylene-bis-(phenylisocyanate) (4,4'-MDI and 2,4'-MDI) and the like. In the preparation of polyurethane and polyurethane/urea elastomers, the aromatic diisocyanates are reacted with a long chain (high molecular weight) polyol to produce a prepolymer containing free isocyanate groups. This prepolymer may then be chain extended with a short chain (low
25 molecular weight) polyol or aromatic diamine to form a polyurethane or polyurethane/urea elastomer (which is known generically as polyurethane or urethane). A liquid mixture of prepolymer and curative polymerizes, increasing steadily in viscosity until finally a solid elastomer is formed. Among the chain extenders or cross-linking agents (curatives) used, primary and secondary polyalcohols, aromatic diamines, and in
30 particular, 4,4'-methylene-bis(2-chloroaniline), i.e. MBOCA, are most common. The use

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of MBOCA allows the manufacture of urethane elastomers with good mechanical properties and acceptable processing times.

- Although MBOCA is the most widely used chain-extender in the production of castable polyurethanes, it suffers from the disadvantage of decomposition at high temperatures, as well as being quite toxic and Ames positive. These negative features of MBOCA have prompted those in the polyurethane art to investigate alternate materials as chain-extenders. Examples of other amines that have been used include 3,3',5,5'-tetraisopropyl-4,4'-diaminodiphenylmethane and 3,5-dimethyl-3',5'-diisopropyl-4,4'-diaminophenylmethane, 3,5-diethyl-2,4-toluenediamine and/or 3,5-diethyl-2,6-toluenediamine (i.e. DETDA), 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline), 3,5-dimethylthio-2,4-toluenediamine, 3,5-dimethylthio-2,6-toluenediamine, and 3,5-diamino-4-chlorobenzoic acid-isobutylester. While these amines do function as cross-linking agents, the resultant pot life of the polymer mixture is so short that a reasonable processing time for cast elastomers is not possible.
- Another curing agent used in the manufacture of polyurethanes is methylene dianiline (MDA). Methylene dianiline is well-known to those skilled in the art as a good curative if there is only aliphatic diisocyanate present. It results in a much shorter pot life than MBOCA. This short pot life is exacerbated by the presence of toluene diisocyanate (TDI). There are also toxicity issues related to the use of MDA.
- Another chain-extending agent for polyurethanes is 4,4'-methylene-bis(3-chloro-2,6-diethylaniline) (MCDEA, commercially available as Lonzacure from the Lonza Corporation). This curative material is reportedly lower in toxicity but it reacts with isocyanates much faster than MBOCA does. (See Th. Voelker et al, Journal of Elastomers and Plastics, 20, 1988 and ibid, 30th Annual Polyurethane Technical/Marketing Conference, October, 1986.) Although this curative does react with isocyanate-terminated prepolymers (including TDI-based prepolymers or 2,4'-MDI-based prepolymers) to give elastomers with desirable properties, they have a tendency to crack when undergoing polymerization.

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The amount and presence of free, unreacted TDI monomer has other deleterious effects on the processing and manufacture of urethanes. A major problem with mono-nuclear aromatic diisocyanates, such as toluenediisocyanate, is that they are toxic and because of their low molecular weight, they tend to be quite volatile. Therefore, 2,4'-MDI-based
5 prepolymer have much better health and safety aspects. Pure 4,4'-MDI-based prepolymer cured with amines, however, are much to fast.

U.S. Patent 5,077,371 discloses a prepolymer that is low in free TDI. U.S. Patent 4,182,825 also describes polyether based prepolymer made from hydroxy terminated polyethers capped with toluene diisocyanate, in which the amount of unreacted TDI is
10 substantially reduced. These prepolymer can be further reacted with conventional organic diamines or polyol curatives to form polyurethanes. When combining the teachings of this patent with the use of MCDEA as a chain extender, the resulting solid elastomer goes through a gel stage having a low strength which can allow cracking of the polymerization mass to occur. Conventional TDI prepolymer with higher levels of free
15 TDI also yield the same unsatisfactory gel state.

Surprisingly, it has been found that certain prepolymer prepared with both 2,4'-MDI and an aliphatic diisocyanate can be used with chain extenders such as 3,5-diamino-4-chlorobenzoic acid isobutylester, to give elastomers with much longer casting time, thus providing more time and/or larger articles and/or a reduced propensity to crack. This
20 phenomena was only known for TDI-based prepolymer prepared with both TDI and an aliphatic diisocyanate (see U.S. Patent 6,046,297). The prepolymer of the present invention also provide extended pour life, and compared to TDI-based prepolymer known in this field, much better health and safety aspects since they are free of toxic TDI. MDI is known to have a much lower vapor pressure than TDI, and thus, is easier and
25 safer to work with. An example of suitable aliphatic diisocyanate for the present invention would be a mixture of the three geometric isomers of 1,1'-methylene-bis-(4-isocyanatocyclohexane), which are abbreviated collectively as "H12MDI." One such mixture of isomers is available commercially and commonly referred to as dicyclohexylmethane-4,4'-diisocyanate. These results are surprising.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been discovered that castable polyurethane elastomers can be formulated with enhanced processing characteristics during the casting operation, including reduced tendency to crack, extended pour life, and which are free of toxic TDI.

The present invention comprises an isocyanate-terminated prepolymer prepared with both 2,4'-MDI and an aliphatic diisocyanate such as an isomeric mixture of 1, 1'-methylene-bis-(4-isocyanatocyclohexane), i.e. H12MDI, with the prepolymer being free of TDI monomer but providing the same curing properties as prepolymers based on TDI. Other examples of suitable aliphatic diisocyanate that may be employed include the various pure geometric isomers of H12MDI; isophorone diisocyanate (IPDI); 1,6-hexamethylene diisocyanate (HDI) and 1,4-cyclohexane diisocyanate (CHDI) and mixtures thereof.

In accordance with the invention, these prepolymer can be then cured with an aromatic diamine curative such as, for example, 3,5-diamino-4-chlorobenzoic acid isobutylester to yield castable urethane articles with the desirable properties of enhanced processing characteristics.

Thus according to an aspect of the present invention as claimed there is provided a polyurethane elastomer comprising the reaction product of: (a) an NCO-terminated prepolymer prepared by reacting: (1) diphenylmethane diisocyanate having a 2,4'-MDI isomer content of greater than 80% by weight, with (2) a high molecular weight polyol selected from the group consisting of polyalkyleneether polyols having a number average molecular weight of 250 to 10,000, polyester polyols having a number average molecular weight of 250 to 10,000 and mixtures thereof, at a temperature of between 30°C and 150°C for a time sufficient to form the NCO-terminated prepolymer, with the OH groups of said polyol being reacted with the NCO groups of said diphenylmethane diisocyanate in a stoichiometric ratio of NCO groups to OH groups in the range of 1.5:1 to 20:1; (b) an aliphatic diisocyanate selected from the group consisting of the isomers of 1,1'-methylene-bis-(4-isocyanatocyclohexane), 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 1,3-xylylene diisocyanate, hexamethylene diisocyanate, the isomers of m-

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tetramethylxylylene diisocyanate (TMXDI), mixtures thereof and prepolymers thereof; and (c) an aliphatic and/or aromatic di- or polyamine; wherein the reactants are present in amounts such that the equivalent ratio of NCO groups to the sum of NCO-reactive groups of the resultant elastomer is in the range of from 0.8:1 to 1.2:1.

- 5 According to another aspect of the present invention as claimed there is provided a process for the production of polyurethane elastomers comprising: (A) reacting (a1) diphenylmethane diisocyanate having a 2,4'-isomer content of greater than 80% by weight with (a2) a high molecular weight polyol selected from the group consisting of polyalkyleneether polyols having a number average molecular weight of 250 to 10,000,
- 10 polyester polyols having a number average molecular weight of 250 to 10,000 and mixtures thereof, at a temperature of between 30°C and 150°C for a time sufficient to form an NCO-terminated prepolymer, with the OH groups of said polyol being reacted with the NCO groups of said diphenylmethane diisocyanate in an equivalent ratio of NCO groups to OH groups in the range of 1.5:1 to 20:1; (B) adding (b) an aliphatic
- 15 diisocyanate selected from the group consisting of the isomers of 1,1'-methylene-bis-(4-isocyanatocyclohexane), 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 1,3-xylylene diisocyanate, hexamethylene diisocyanate, the isomers of 1,1,4,4-tetramethylxylylene diisocyanate, mixtures thereof and prepolymers thereof, to the NCO-terminated prepolymer formed in step (A); and (C) reacting the mixture from step (B)
- 20 with (c) an aliphatic and/or aromatic di- or polyamine, in a sufficient amount to effectively cure the polyurethane; wherein the reactants are present in amounts such that the equivalent ratio of NCO groups to the sum of NCO-reactive groups of the resultant elastomer is in the range of from 0.8:1 to 1.2:1.

- 25 These and other aspects and embodiments of the invention are described below and in the claims that follow.

DETAILED DESCRIPTION OF THE INVENTION

In the practice of this invention, an organic diisocyanate, such as 2,4'-MDI, is reacted with high molecular weight polyesters and/or polyether polyols to produce a prepolymer. Preferably, the organic diisocyanate comprises an isomeric mixture of diphenylmethane

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diisocyanate in which the quantity of the 2,4'-MDI isomer is present in an amount of greater than 80% by weight, preferably greater than 90% by weight, and most preferably greater than 97% by weight. The advantage here is that no purifying step (e.g. to remove free isocyanate) has to be carried out.

- 5 High molecular weight polyols, including specifically polyether polyols and/or polyester polyols which have a number average molecular weight of at least 250, are used to prepare the prepolymer of the instant invention. Molecular weight of the polyols is preferably from about 500 to 4000, with molecular weights of 1000 to 2000 being the most preferred. However, the molecular weight of the high molecular weight polyol may
 10 be as high as 10,000. Thus, these polyols may have a molecular weight ranging between any combination of these upper and lower values, inclusive, e.g. from 250 to 10,000, preferably from 500 to 4000 and most preferably from 1000 to 2000.

The preferred polyalkyleneether polyols of the invention may be represented by the general formula:



wherein:

R represents an alkylene radical,

and

- 20 n represents an integer large enough such that the resultant polyether polyol has a number average molecular weight of at least 250, preferably at least 500.

These polyalkyleneether polyols are well-known components of polyurethane products and can be prepared by, for example, the polymerization of cyclic ethers (such as alkylene oxides) and glycols, dihydroxyethers, and the like by known methods.

- 25 The polyester polyols are typically prepared by the reaction of dibasic acids (usually adipic acid but other components, such as glutaric acid, sebacic acid, or phthalic acid,

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may also be present) with diols such as ethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, diethylene glycol, 1,6-hexanediol, and the like where linear polymer segments are required. Units of higher functionality such as glycerol, trimethylolpropane, pentaerythritol, sorbitol, and the like may be employed with either polyester polyols or
5 polyether polyols if chain branching or ultimate cross-linking is sought.

Some polyester polyols employ caprolactone and dimerized unsaturated fatty acids in their manufacture. Another type of polyester polyol of interest is that obtained by the addition polymerization of ϵ -caprolactone in the presence of an initiator. Still other polyols that can be used are those having at least two hydroxyl groups and whose basic
10 backbone is obtained by polymerization or copolymerization of such monomers as butadiene and isoprene monomers.

Preferred polyols of the current invention are polyalkylene ethers. Most preferred polyols of this group of compounds include polytetramethylene ether glycols (PTMEG).

Polycarbonate polyols can also be used.

15 The total polyol blend portion of the instant invention can be a combination of high molecular weight polyol, as previously described, and low molecular weight polyol. An aliphatic glycol is the preferred low molecular weight polyol. Suitable aliphatic polyols are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, neopentyl glycol, 1,3-butanediol, 1,4-
20 butanediol, and the like.

The most preferred low molecular weight polyol is diethylene glycol. In general, the weight of the low molecular weight polyol should be no more than 20% by weight of the combined weight of high molecular weight polyol and low molecular weight polyol. The preferred weight range is 0 to 15% by weight of the combined weight; and more preferred
25 is 0-8% by weight of the combined weight.

The 2,4'-MDI-based prepolymers are prepared by dissolving or melting 2,4'-MDI used with any other conventional diisocyanates that may optionally be used, adding the polyol or polyol blend, and maintaining the temperature from room temperature to temperatures

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as high as 150°C for the necessary time period to react all the available hydroxyl groups. Preferred reaction temperatures are from 30°C to 100°C, inclusive; and more preferred are from 50°C to 85°C, inclusive.

Alternatively, the polyol can be provided, and the isocyanate is added thereto.

- 5 Once the 2,4'-MDI prepolymer is formed, an aliphatic diisocyanate such as, e.g. H12MDI, and/or a prepolymer prepared from an aliphatic diisocyanate, is then added to the formed 2,4'-MDI prepolymer.

- If an aliphatic diisocyanate monomer is to be added to the prepolymer, the preferred monomer is H12MDI or another aliphatic diisocyanate monomer of comparatively high
10 molecular weight, low volatility, and low toxicity. If more volatile aliphatic diisocyanates such as, for example 1,4-cyclohexane diisocyanate (CHDI), isophorone diisocyanate (IPDI) and/or hexamethylene diisocyanate (HDI)) are employed, it is preferred that they be employed as the prepolymers to reduce their volatility. More preferably, the prepolymers of such volatile aliphatic diisocyanates as CHDI, HDI and/or IPDI should
15 contain below about 0.4% by weight of free unreacted monomer. If necessary, free monomer can be removed by use of conventional separation techniques such as extraction, distillation, or absorption.

- If a prepolymer prepared from H12MDI (or other aliphatic diisocyanate) is to be added to the 2,4'-MDI prepolymer, the H12MDI prepolymer may be prepared in a manner similar
20 to that for the 2,4'-MDI prepolymer. However, because of the slower reactivity with polyols of H12MDI versus 2,4'-MDI, higher reaction temperatures are employed. Preferred temperatures are 70°C to 140°C; more preferred are from 80°C to 130°C. Free H12MDI may optionally be removed from the prepolymer by the traditional separation processes previously mentioned.

- 25 In preparing a prepolymer with either aromatic or aliphatic diisocyanates, the stoichiometric ratio of isocyanate groups to hydroxyl groups in the reactants should preferably be from 1.5:1 to 20:1, although somewhat lower and higher ratios are permissible. When the ratio is much lower, the molecular weight of the isocyanate-

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terminated polyurethane becomes so large that the viscosity of the mass makes mixing of chain extenders into the prepolymer considerably more difficult. A ratio of two (2) isocyanate groups to one (1) hydroxyl group is the theoretical ratio for the end-capping of a difunctional polyalkyleneether or ester polyol with a diisocyanate. An excess ratio
5 approaching the 20:1 ratio will result in high levels of free diisocyanate in the mixture, which must be subsequently removed at greater cost. The preferred range is from 1.7:1 to 4:1 for prepolymers of 2,4'-MDI, and from 2:1 to 12:1 for prepolymers of H12MDI or other aliphatic diisocyanates.

Representative aliphatic diisocyanates include, but are not limited to, the following, as
10 examples: hexamethylene diisocyanate (HDI); 1,3-xylylene diisocyanate (XDI); 1,1,4,4-tetramethylxylylene diisocyanate in its para- or meta-isomer forms (p-TMXDI, m-TMXDI); isophorone diisocyanate (IPDI); 1,4-cyclohexane diisocyanate (CHDI); and the geometric isomers of 1,1'-methylene-bis-4(-isocyanatocyclohexane) (H12MDI). Preferred diisocyanates include H12MDI, CHDI, and IPDI. More preferred diisocyanates include
15 H12MDI in its various isomeric forms, mixed or pure.

It is desired that about 30-95% by weight of the isocyanate content of the final prepolymer be from the aromatic isocyanate monomer or prepolymer of the final composition, such as 2,4'-MDI. About 5-70% by weight of the isocyanate content of the final prepolymer should be from the aliphatic isocyanate monomer or prepolymer, for
20 example, H12MDI. The sum of the isocyanate content from the aromatic isocyanate monomer and of the isocyanate content from the aliphatic isocyanate monomer totals 100% by weight

The curative used for the prepolymer can be selected from a wide variety of conventional and well known organic diamine or polyol materials. Preferred materials are the aromatic
25 diamines which are either low melting solids or liquids. Specifically preferred are the diamines, polyols, or blends thereof having a melting point below 120°C. These diamines or polyols are generally the ones presently used in the industry as curatives for polyurethane. The selection of a curative is generally based on reactivity needs, property

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needs for a specific application, process condition needs, and pot life desired. Known catalysts may be used in conjunction with the curative.

As previously mentioned, the most preferred curative is MBOCA, 3,5-diamino-4-chlorobenzoic acid isobutylester, MCDEA, or mixtures thereof. Other curatives, such as

5 diethyltoluene diamine (DETDA), tertiary butyl toluene diamine (TBTDA), dimethylthio-toluene diamine (i.e. Ethacure™ 300 from Albemarle Corporation), trimethylene glycol di-p-amino- benzoate (i.e. Polacure™ 740 from Air Products and Chemicals Inc.), and 1,2-bis(2-aminophenylthio)ethane (i.e. Cyanacure from American Cyanamid Company) can be used in addition to the aforementioned preferred curatives.

10 For curing these prepolymers, the number of - NH₂ (amine) groups in the aromatic diamine component should be approximately equal to the number of - NCO (isocyanate) groups in the prepolymer. A small variation is permissible but in general from about 80 to 120% of the stoichiometric equivalent should be used, and preferably from about 85 to 100%.

15 The reactivity of isocyanato groups with amino groups varies according to the structure to which the groups are attached. As is well known, as described in, for example, U.S. Patent 2,620,516, the disclosure of which is hereby incorporated by reference, some amines react very rapidly with some isocyanates while others react more slowly. In the latter case, it is optional to use catalysts to cause the reaction to proceed fast enough to

20 make the product non-sticky within 30-180 seconds. However, more often it is preferable that the prepolymer/curative blend remains flowable (i.e. below 50 poise) for at least 120 seconds and more preferably for at least 180 seconds.

For some of the aromatic diamines, the temperature of the reaction or of the polyurethane reactants will need only be controlled in order to obtain the proper reaction time; thus, for

25 a diamine that ordinarily would be too reactive, a catalyst would be unnecessary; and a lowering of the reaction temperature would suffice. A great variety of catalysts are available commercially for accelerating the reaction of the isocyanato groups with compounds containing active hydrogen atoms (as determined by the well-known Zerewitinoff test). It is well within the skill of one of ordinary skill in this field to select

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catalysts to fit particular needs and adjust the amounts used to further refine the conditions. Adipic acid, oleic acid and triethylene diamine (commercially available under the trademark Dabco™ from AirProducts and Chemicals, Inc.) are typical of suitable catalysts.

- 5 The polyurethanes and the prepolymers used can be additionally stabilized using auxiliary agents such as acid stabilizers, e.g. chloropropionic acid, dialkylphosphates, p-toluene sulfonic acid, or acid chlorides, e.g. benzoic acid chloride, phthalic acid dichloride, and antioxidants, e.g. Ionol® and Stabaxol®, phosphites and further stabilizers generally known in the art. The stabilizers are used in amounts smaller than 0.5 wt. % (based on the
- 10 total amount of the polyurethane or the prepolymer used).

The resultant urethane products are suitable for industrial applications that require durable physical and mechanical properties in the final elastomers. Industrial rolls such as paper mill rolls, industrial wheels, and industrial tires are some examples of applications that require such properties.

- 15 The following examples are meant for illustrative purposes only and are not intended to limit the scope of this invention in any manner whatsoever.

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EXAMPLES:

The following materials were used in the working examples:

- Isocyanate 1: a liquid diphenylmethane diisocyanate containing about 97% by weight of the 2,4'-isomer of MDI
- 5 Isocyanate 2: dicyclohexylmethane-4,4'-diisocyanate having an NCO group content of about 32% by weight
- Polyol 1: polytetrahydrofuran, a polyether polyol having an OH number of 112 mg KOH/g polyol, which is commercially available as Terathane® 1000 from Invista
- 10 Polyol 2: a polyesterpolyol having an OH-number 56 mg KOH/g polyol, and which is prepared from adipic acid and ethyleneglycol
- Amine 1: 3,5-diamino-4-chlorobenzoic acid isobutyl ester, an amine curing agent

Preparation of Prepolymers :

- Isocyanate 1 was stirred at 50°C under dry nitrogen. Polyol was added, and the mixture
- 15 was stirred for 3-6 hours at approximately 80°C. The NCO content was measured.

Details concerning the amounts of Isocyanate 1 and Polyols used are set forth in Table 1, as are measured data for the resultant Prepolymers.

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Table 1 (comparative prepolymers):

Example	Isocyanate 1 [wt.-%]	Polyol 1 [wt.-%]	Polyol 2 [wt.-%]	Stirring time in hours	NCO [wt.-%]	Viscosity at 70°C [mPas]
Prepolymer A1	29.53%	70.47%	---	3	3.81%	2600
Prepolymer A2	34.29%	65.71%	---	3	5.86%	1140
Prepolymer A3	39.06%	60.94%	---	3	7.79%	670
Prepolymer A4	21.54%	---	78.46%	4	3.98%	3200

Preparation of Prepolymers (according to the invention):

The prepolymer A1 or A4 was stirred for 1 hour at 80°C under dry nitrogen with

- 5 Isocyanate 2. The respective quantities of components used and measured data of the resultant prepolymers are set forth in Table 2.

Table 2 (prepolymers according to the invention):

Example	Prepolymer [wt.-%]	Isocyanate 2 [wt.-%]	NCO [wt.-%]	Viscosity at 70°C [mPas]
Prepolymer B 1	92.81% of A 1	7.19%	5.79%	1942
Prepolymer B 2	85.45% of A 1	14.55%	7.86%	1356
Prepolymer B 3	78.45% of A 1	21.44%	9.82%	973
Prepolymer B 4	92.63% of A 4	7.37%	5.95%	2270
Prepolymer B 5	85.58% of A 4	14.42%	7.94%	1490

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Preparation of Cast Elastomers using the Prepolymers:

- All cast elastomers were prepared using Amine 1 as the curing agent. The prepolymer was stirred at 90°C while degasing until bubble free, and Amine 1 at 100°C was added
- 5 while stirring was continued for 30 sec. The mixture was poured into an open mold heated to a temperature of 110°C and cured for 24 hours at 110°C.

The amounts and results are shown in Tables 3 and 4.

Table 3 (comparative cast elastomers):

Example		1*	2*	3*	4*
Prepolymer		A3	A2	A1	A4
Amount of Prepolymer (parts by weight)		100	100	100	100
Amount of Amine 1 (parts by weight)		20	15	10	10
casting time	[sec]	150	270	500	210
mechanical properties					
Shore A (DIN 53505)		99	97	91	92
Shore D (DIN 53505)		54	45	34	35
Stress at 100% Strain (DIN 53504)	[MPa]	17.37	12.37	8.13	7
Stress at 300% Strain (DIN 53504)	[MPa]	28.23	19.53	10.97	12
Ultimate Tensile Strength (DIN 53504)	[MPa]	38.17	39.98	28.56	45
Elongation at Break (DIN 53504)	[%]	395	481	603	680
Graves (DIN 53515)	[kN/m]	119	89	60	79
Rebound Resilience (DIN 53512)	[%]	49	46	52	43
Abrasion (DIN 53516)	[cbmm]	56	49	46	70
Compression Set 22°C (DIN 53517)	[%]	37.8	30	26.2	22
Compression Set 70°C (DIN 53517)	[%]	63.4	60.9	44.3	44

*comparative examples

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Table 4 (cast elastomers according to the invention):

Example		5	6	7	8	9
Prepolymer		B1	B2	B3	B4	B5
Amount of Prepolymer (parts by weight)		100	100	100	100	100
Amount of Amine 1 (parts by weight)		15	20	25	15	20
casting time	[sec]	420	465	540	240	285
mechanical properties						
Shore A (DIN 53505)		96	99	96	98	99
Shore D (DIN 53505)		43	59	43	48	58
Stress at 100% Strain (DIN 53504)	[MPa]	10.35	16.46	23.75	19.04	26.31
Stress at 300% Strain (DIN 53504)	[MPa]	17.24	31.86	17.24	33.49	-
Ultimate Tensile Strength (DIN 53504)	[MPa]	30.49	32.68	32.38	34.27	33.07
Elongation at Break (DIN 53504)	[%]	467	304	213	314	170
Graves (DIN 53515)	[kN/m]	73	86	119	91	94
Rebound Resilience (DIN 53512)	[%]	43	50	43	50	50
Abrasion (DIN 53516)	[cbmm]	63	66	63	60	72
Compression Set 22°C (DIN 53517)	[%]	42.8	69.2	71.9	72.0	53.9
Compression Set 70°C (DIN 53517)	[%]	65.4	93.6	94.4	72.1	83.0

As can be seen from Tables 3 and 4, the pouring time in Example 1* was only 150 seconds whereas in Example 6, the pouring time could be increased up to 465 seconds. In Example 5, the pouring time was 420 seconds compared to only 270 seconds in Example 2*. A longer pouring time allows larger and more complex parts to be prepared.

In Example 7 the pouring time was 540 seconds despite the fact that the prepolymer has a high NCO content, i.e. 9.82%. With the inventive prepolymers, one can prepare elastomers with a high hardness which simultaneously have a long pouring time.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations

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can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" or "comprising", will be
5 understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that that prior publication (or information derived from
10 it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A polyurethane elastomer comprising the reaction product of:
 - (a) an NCO-terminated prepolymer prepared by reacting:
 - (1) diphenylmethane diisocyanate having a 2,4'-MDI isomer content of greater than 80% by weight,
 - with
 - (2) a high molecular weight polyol selected from the group consisting of polyalkyleneether polyols having a number average molecular weight of 250 to 10,000, polyester polyols having a number average molecular weight of 250 to 10,000 and mixtures thereof,

at a temperature of between 30°C and 150°C for a time sufficient to form the NCO-terminated prepolymer, with the OH groups of said polyol being reacted with the NCO groups of said diphenylmethane diisocyanate in an stoichiometric ratio of NCO groups to OH groups in the range of 1.5:1 to 20:1;
 - (b) an aliphatic diisocyanate selected from the group consisting of the isomers of 1,1'-methylene-bis-(4-isocyanatocyclohexane), 1,4-cyclohexane diisocyanate, isophorone diisocyanate 1,3-xylylene diisocyanate, hexamethylene diisocyanate, the isomers of m-tetramethylxylylene diisocyanate (TMXDI), mixtures thereof and prepolymers thereof;
- and
- (c) an aliphatic and/or aromatic di- or polyamine;

wherein the reactants are present in amounts such that the equivalent ratio of NCO groups to the sum of NCO-reactive groups of the resultant elastomer is in the range of from 0.8:1 to 1.2:1.

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2. A polyurethane elastomer according to Claim 1, wherein (c) said di- or polyamine is selected from the group consisting of 4,4'-methylene-bis-(2-chloroaniline), 3,5-diamino-4-chlorobenzoic acid isobutyl ester and 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline).

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3. A process for the production of polyurethane elastomers comprising:

(A) reacting

(a1) diphenylmethane diisocyanate having a 2,4'-isomer content of greater than 80% by weight

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with

(a2) a high molecular weight polyol selected from the group consisting of polyalkyleneether polyols having a number average molecular weight of 250 to 10,000, polyester polyols having a number average molecular weight of 250 to 10,000 and mixtures thereof,

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at a temperature of between 30°C and 150°C for a time sufficient to form an NCO-terminated prepolymer, with the OH groups of said polyol being reacted with the NCO groups of said diphenylmethane diisocyanate in an equivalent ratio of NCO groups to OH groups in the range of 1.5:1 to 20:1;

20 (B) adding

(b) an aliphatic diisocyanate selected from the group consisting of the isomers of 1,1'-methylene-bis-(4-isocyanatocyclohexane), 1,4-cyclohexane diisocyanate, isophorone diisocyanate, 1,3-xylylene diisocyanate, hexamethylene diisocyanate, the isomers of 1,1,4,4-tetramethylxylylene diisocyanate, mixtures thereof and prepolymers thereof,

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to the NCO-terminated prepolymer formed in step (A);

and

(C) reacting the mixture from step (B) with

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- (c) an aliphatic and/or aromatic di- or polyamine, in a sufficient amount to effectively cure the polyurethane;

wherein the reactants are present in amounts such that the equivalent ratio of NCO groups to the sum of NCO-reactive groups of the resultant elastomer is in the range of from 0.8:1 to 1.2:1.

4. A process of Claim 3, wherein (c) said di- or polyamine is selected from the group consisting of 4,4'-methylene-bis(2-chloroaniline), 3,5-diamino-4-chlorobenzoic acid isobutyl ester and 4,4'-methylene-bis(3-chloro-2,6-diethylaniline).

5. Polyurethane elastomers prepared by a process according to claim 3 or 4.

6. Polyurethane elastomers, processes for their production and/or uses thereof substantially as herein described with reference to the Examples (excluding the comparative Examples).