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(54) Title: POLYCARBAMATES, PROCESS FOR PREPARING POLYCARBAMATES, AND PROCESS FOR PREPARING POLYISOCYANATES

(57) Abstract

Polycarbamates of a polyisocyanate and secondary alcohols are disclosed. These carbamates are characterized in being readily pyrolyzed to form the corresponding polyisocyanate and alcohol with low formation of tars and other by-products. Thus, these polycarbamates can be pyrolyzed under relatively mild conditions, and in the absence of solvent and catalyst.

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POLYCARBAMATES, PROCESS FOR PREPARING POLYCARBAMATES, AND PROCESS FOR PREPARING POLYISOCYANATES

This invention relates to a process for preparing polyisocyanates such as are useful, for example, in making polyurethane polymers.

Polyisocyanates are commonly used in various applications, the most common of which is the preparation of polyurethane polymers. The most commercially important of these are aromatic polyisocyanates such as toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) and the so-called polymeric MDI products which are usually formed as by-products in MDI production. However, certain aliphatic polyisocyanates are also used commercially, such as hexamethylene diisocyanate, isophorone diisocyanate and hydrogenated MDI (H_{12} MDI).

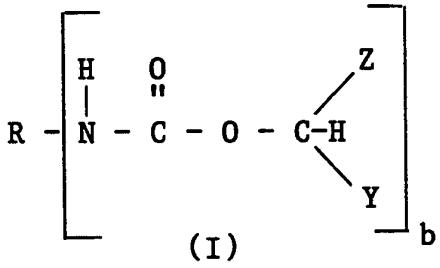
On a commercial scale, polyisocyanates are almost universally produced by reacting the corresponding polyamine with phosgene. For example, TDI is produced by reacting phosgene with toluene diamine. Several problems are associated with this process, the most significant of which is that large quantities of phosgene must be handled Phosgene is highly toxic, and its handling requires special care to prevent exposure to workers. HCl is produced in the reaction of the phosgene and the polyamine, and must be neutralized or otherwise removed. The phosgene and HCl also engage in various side reactions, producing unwanted chlorinated by-products which affect the quality and purity of the product polyisocyanates. Thus, a process by which polyisocyanates can be prepared without using phosgene would be highly desirable.

Several non-phosgene routes to polyisocyanates have been developed. One such route involves the preparation of an n-alkyl biscarbamate, which is subsequently pyrolyzed to form the corresponding polyisocyanate and alcohol. The biscarbamate is generally prepared by one of two methods. The first such method involves the oxidative carbonylation of an amine with carbon monoxide, oxygen and an alcohol such as ethanol or methanol, to form the corresponding ethyl- or methylcarbamate. The other method involves a reductive carbonylation of a nitro compound with carbon monoxide and an alcohol such as ethanol or methanol to form the corresponding ethyl- or methylcarbamate. See, for example, WO 86-05179.

In these processes, the ethyl- or methylpolycarbamates are pyrolyzed at high temperatures and under reduced pressures. At these temperatures, the polyisocyanates often polymerize as they form, producing tars and other by-products. For this reason, and because these carbamates are often crystalline, a solvent is required as a diluent The use of a solvent in the pyrolysis adds costs in recovering the product polyisocyanate from the solvent. To a lesser extent, the high temperature required further increases the cost of these processes.

Thus, it would be desirable to provide a route to make polyisocyanates through a polycarbamate intermediate, wherein the pyrolysis of the polycarbamate can be conducted in the absence of solvent, and preferably at moderate temperatures.

In one aspect this invention is a polycarbamate as represented by the structure (I)



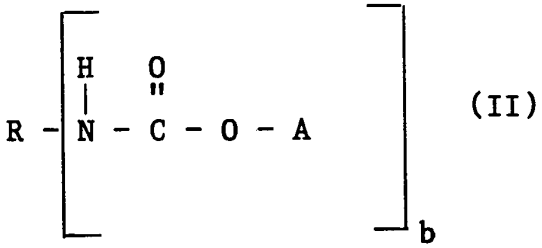
(I)

wherein b is a number of two or more, R is an organic radical with a valence equal to b, Y is a group having at least two carbon atoms, and Z is an aliphatic or aromatic group containing at least one carbon atom.

In another aspect, this invention is a process for preparing a polyisocyanate, comprising pyrolyzing the polycarbamate of the first aspect under reduced pressure and at a temperature of 150 to 270°C, to form the corresponding polyisocyanate and alcohol.

In a third aspect, this invention is a process for preparing a polyisocyanate, comprising forming a polycarbamate of the first aspect, and then pyrolyzing the polycarbamate under reduced pressure and at a temperature of 150 to 270°C, to form the corresponding polyisocyanate and alcohol.

In a fourth aspect, this invention is a process for preparing a polycarbamate comprising reacting a polycarbamate represented by the structure (II)



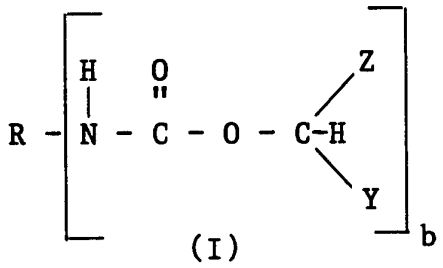
(II)

wherein A is C_{1-6} linear alkyl with a secondary alcohol represented by the structure Z-CH(OH)-Y, at an elevated temperature such that the polycarbamate represented by structure (I) and an alcohol of the structure A-OH are formed, and wherein the alcohol A-OH is removed from the product polycarbamate continuously or intermittently as it forms.

Unexpectedly, the polycarbamate of this invention can be pyrolyzed to form the corresponding polyisocyanate under surprisingly mild conditions, compared to those required to pyrolyze ethyl- or methylpolycarbamates. Thus, the pyrolysis can be conducted at lower temperatures than required to pyrolyze ethyl- or methylpolycarbamate, and also can be

conducted neat and without solvent. In addition, the polycarbamates can be pyrolyzed in the substantial absence of solvent with greatly reduced formation of tar and other by-products, compared to those formed in the neat pyrolysis of ethyl- or methylpolycarbamates. Since no solvents are needed, the isolation of the isocyanate and the alcohol can be greatly simplified.

The polycarbamate of this invention is a compound represented by the structure



(I)

wherein b is a number of two or more, R is a organic radical with a valence equal to b, Y is a a group having at least two carbon atoms, and Z is an aliphatic or aromatic group containing at least one carbon atom.

In structure (I), "b" is preferably a number from two to four, more preferably from two to three, most preferably two.

"R" is preferably a hydrocarbon radical, which may be aliphatic, alicyclic, or aromatic. Suitable aliphatic hydrocarbon radicals include straight chain or branched hydrocarbons having from two, preferably from 4 carbon atoms, to 20, preferably 12, more preferably 8 carbon atoms. Most preferred are linear hydrocarbon diradicals having from 4 to 8 carbon atoms. Examples of such include tetramethylene, pentamethylene, hexamethylene, and octamethylene diradicals. Suitable alicyclic hydrocarbon radicals include monocyclic and polycyclic hydrocarbons, preferably monocyclic hydrocarbons having from 6 to 16 carbon atoms. Among these preferred alicyclic hydrocarbon radicals are cyclohexane, alkyl-substituted cyclohexane, isophorone dialkyl-substituted cyclohexane, mono- or dihalo-substituted cyclohexane, cyclooctane, alkyl-substituted cyclooctane, dialkyl-substituted cyclooctane, mono- or dihalo-substituted cyclooctane, bis(cyclohexyl)alkanes such as methylene bis(cyclohexane) and propylidene bis(cyclohexane), and like radicals. Suitable aromatic polyradicals include polyradicals of benzene, toluene and other monoalkyl benzenes, o-, p-, and m-xylene and other dialkyl benzenes, diphenylalkanes such as diphenyl methane and 2,2-diphenylpropane, and halogenated aromatics.

Most preferred R radicals are hexamethylene, phenylene, diphenylmethane, toluene, cyclohexane, xylenyl, methylcyclohexane, isophorone and dicyclohexylmethane radicals.

In structure (I), exemplary "Z" groups include linear or branched alkyl, cycloalkyl, alkoxy-substituted alkyl, benzyl, phenyl or other aromatic group, which may be substituted, and like groups. Preferred Z groups include C_1-C_4 straight chain alkyl, C_3-C_6 branched alkyl,

alkyl ether, phenyl and benzyl. More preferably, the Z group is methyl, ethyl, C_3-C_6 secondary alkyl, C_4-C_6 tertiary alkyl, phenyl or benzyl.

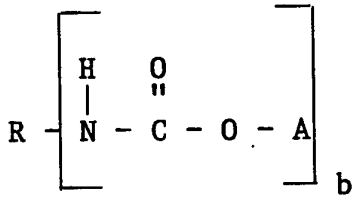
Exemplary Y groups include those having from 2 to 20, preferably 3 to 6 carbon atoms, and are represented by the structure

$$-CR^1R^2R^3$$

wherein R^1 and R^2 are hydrogen, C_1-C_6 alkyl, aromatic, benzyl, alkoxy or phenoxy and R^3 is C_1-C_6 alkyl, aromatic, benzyl, alkoxy, phenoxy or dialkylamine. R^1 is preferably hydrogen, C_1-C_6 alkyl or phenyl. R^2 is preferably C_1-C_6 alkyl, phenyl or C_1-C_4 alkoxy. If R^1 and R^2 are both hydrogen, R^3 may be C_1-C_6 alkyl, phenyl, alkoxy, phenoxy or dialkylamine, but in that case it is preferred that R^3 is C_1-C_4 alkoxy or phenoxy, more preferably methoxy or ethoxy. Otherwise, R^3 is preferably C_1-C_4 alkyl, phenyl or C_1-C_2 alkoxy, more preferably methyl, ethyl, methoxy or ethoxy.

Of particular interest are Y groups in which R^1 and R^2 are hydrogen and R^3 is ethoxy or methoxy; R^1 and R^2 are hydrogen and R^3 is methyl, ethyl or phenyl; R^1 is hydrogen and R^2 and R^3 are each methyl, ethyl or phenyl; R^1 is hydrogen, R^2 is methyl, ethyl or phenyl and R^3 is methoxy or ethoxy; R^1 and R^2 are both methyl, ethyl or phenyl and R^3 is methoxy or ethoxy; and R^1, R^2 and R^3 are all methyl or ethyl.

The polycarbamate of this invention can be prepared in a transesterification reaction involving a polycarbamate as represented by the structure



(II)

and an alcohol having the structure Z-CH(OH)-Y, wherein R, b, Y, and Z are as defined before and A is C_1-C_4 linear alkyl, preferably ethyl or methyl.

The transesterification reaction is conducted at an elevated temperature. In general, a temperature from 50 to 250°C can be used, with faster reaction occurring at higher temperatures. As the reaction proceeds, an alcohol corresponding to the formula A-OH is produced. In order to drive the transesterification to completion, it is preferred to remove the alcohol A-OH from the product as the alcohol is formed. A simple way to accomplish this is to vent alcohol vapors. For this reason, it is preferred to conduct the reaction at a temperature above the boiling point of the alcohol A-OH.

The preferred temperature also depends on whether a catalyst is used to enhance the rate of the transesterification reaction. When a catalyst is used, it is preferred to use a

moderate temperature, that is from 50 to 150°C. When no catalyst is used, a temperature of from 100 to 250°C is preferred.

The transesterification reaction may be run in the presence of a diluent. The diluent advantageously has a boiling point in the temperature range at which the transesterification reaction is conducted, and the reaction is conducted under reflux conditions. The diluent may be any liquid in which the starting and product polycarbamates do not undesirably react. Suitable such diluents include aromatic solvents such as toluene and benzene, ethyl acetate, methylene chloride, acetone, and preferably the alcohol A-OH such as is formed during the transesterification reaction. Preferred solvents are those such as toluene, benzene and ethyl acetate which facilitate removal of the alcohol A-OH from the reaction mixture.

As mentioned before, a catalyst may be used in the transesterification reaction. Suitable catalysts include organometallic catalysts such as organotin, organotitanium, organomercury, organobismuth and similar compounds, with organotin compounds and titanium (IV) compounds being preferred. Suitable organotin compounds include those commonly employed as polyurethane catalysts, including, for example, tin octoate and dialkyl tin dialkanoates such as dimethyltin dilaurate and dibutyltin dilaurate. A suitable titanium (IV) compound is titanium (IV) isopropoxide. Conventional transesterification catalysts such as acids and bases can also be used. Exemplary acids include toluene sulfonic acid, sulfuric acid, and methanesulfonic acid. Exemplary bases include trialkyl amines and alkali metal alkoxides such as sodium or potassium methoxide.

The transesterification is conducted by contacting the polycarbamate starting material with the alcohol Z-CH(OH)-Y and heating them to a temperature as described above. An excess of the alcohol is preferably used in order to drive the reaction to completion. The catalyst, if used, is advantageously present in an amount from 0.01 to 5, preferably 0.1 to 1 weight percent, based on the weight of the starting polycarbamate. Product alcohol A-OH is preferably removed from the reaction mixture as it is formed, in order to drive the equilibrium towards the product polycarbamate. The alcohol Z-CH(OH)-Y can also be replenished as it is consumed, for the same reason. Depending on the temperature used, the reaction proceeds to 90 percent or higher yield in a period of 1 to 30 hours.

After the reaction, it is preferred to work up the product polycarbamate by stripping off volatile impurities and removing residual catalyst and starting polycarbamate though a suitable technique such as solvent extraction or recrystallization.

The starting polycarbamate can itself be prepared in an oxidative or reductive carbonylation of a polyamine of the formula $R\text{-}NH2_b$, wherein R and b are as defined before. Such processes are described, for example, in Japanese Patent (Kokai) Nos. 57-158746-48, 57-70855, 57-185253, and 57-188557. The oxidative carbonylation is advantageously carried out using carbon monoxide, oxygen and an ethanol (to make the polyethylcarbamate) or methanol (to make the polymethylcarbamate). The reductive carbonylation is advantageously carried

out using carbon monoxide and methanol or ethanol, preferably in the presence of a ruthenium catalyst. In either case, the carbonylation is carried out at an elevated temperature and pressure in the presence of an excess of the methanol or ethanol.

A third process for preparing the starting polycarbamate is to oxidatively carbonylate a monoamine or reductive carbonylate a mononitro compound using ethanol or methanol to form a monocarbamate, followed by a coupling of the monocarbamate to form a polycarbamate. This method is particularly suitable for preparing polyaromatic carbamates. For example, a monocarbamate prepared from aniline or nitrobenzene can be coupled via condensation with an aldehyde or ketone to form an alkylene bis- or poly(phenyl carbamate). In such case, the monocarbamate is preferably the methyl or ethyl carbamate of aniline, and the ketone is preferably formaldehyde.

The polycarbamate of this invention can then be pyrolyzed to form the corresponding polyisocyanate. A significant advantage of this invention is that the pyrolysis of these polycarbamates is readily accomplished without the need for solvent or catalyst. In addition, the polycarbamates of this invention form fewer polymeric and tarry by-products upon pyrolysis than do corresponding n-alkyl polycarbamates.

The polycarbamates of this invention are advantageously decomposed into the corresponding polyisocyanate and alcohol by heating at a temperature from 130°C, preferably from 150°C, more preferably from 175°C, to 300°C, preferably to 270°C, more preferably to 250°C, most preferably to 230°C. It is preferred to select a temperature at which the alcohol and the polyisocyanate, which are formed in the pyrolysis, are distilled as they are formed so that an equilibrium between the carbamate and polyisocyanate is not created. It is especially preferred that the temperature be such that both the alcohol and the polyisocyanate, which are formed in the reaction, distill from the reaction mixture as they are formed.

A subatmospheric pressure is preferred in the pyrolysis reaction, preferably from 0.01 to 50 and especially from 0.1 to 5.0 torr, since this facilitates distillation of the alcohol and the polyisocyanate from the reaction mixture.

Although a solvent is not required during the pyrolysis step, one may be used if required. Any solvent can be used which dissolves the polycarbamate, is inert during the pyrolysis and is thermally stable at the temperature used in the pyrolysis reaction. Examples of such solvents include diphenyl oxide, alkylbenzenes, dialkylbenzenes, and secondary alcohols.

In a preferred method, the polycarbamate is first heated to a relatively mild temperature, preferably 50 to 100°C, and maintained at that temperature until the alcohol no longer distills off. This initial heating step is preferably done under vacuum. During this step, a polymeric residue often forms which is believed to contain allophanates and/or polyurethanes. This polymeric residue is then pyrolyzed at higher temperatures, as described above, to recover the polyisocyanate and additional alcohol. The resulting polyisocyanate can be distilled or otherwise purified if needed.

The polyisocyanate prepared in accordance with this invention is useful to prepare polyurethanes, polyureas, polyisocyanurates, polyamides, polyimides and like polymers. Process for preparing these types of polymers from polyisocyanates are well-known and described, for example, in U.S. Patent Nos. 4,876,019, 4,929,646 and 5,010,117, all incorporated herein by reference.

Examples

The following examples are provided to illustrate the invention, but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated.

Example 1

Into a Parr reactor equipped with a vapor phase outlet and a liquid inlet were placed 31.47 parts diphenylmethane dimethyl biscarbamate (MDI dimethyl biscarbamate) and 200 parts 1-methoxy-2-propanol. The mixture was heated to about 220°C with stirring to initiate the transesterification reaction. As the reaction proceeded, about 13 parts per hour of methanol-rich vapor phase was bled from the reactor, and 13 parts per hour of 1-methoxy-2-propanol were added. After about 5 hours, the MDI dimethyl biscarbamate was totally consumed. The product mixture contained 93.4 percent of the MDI di(1-methoxy isopropyl) biscarbamate, and 5.6 percent of an MDI methyl(1-methyoxyisopropyl) biscarbamate.

Example 2

Into a suitable flask equipped with a condenser were placed 68.4 parts diphenylmethane diethyl biscarbamate (MDI diethyl biscarbamate), 180 parts 1-methoxy-2-propanol and 0.5 part dibutyltin dilaurate. The resulting mixture was heated to a temperature ranging from 125 to 145°C. Methanol was removed from the system as the reaction proceeded. After 72 hours, no MDI diethyl biscarbamate remained. The contents of the reaction flask were concentrated and 81.8 parts of MDI di(1-methoxy isopropanol) biscarbamate were obtained.

Example 3

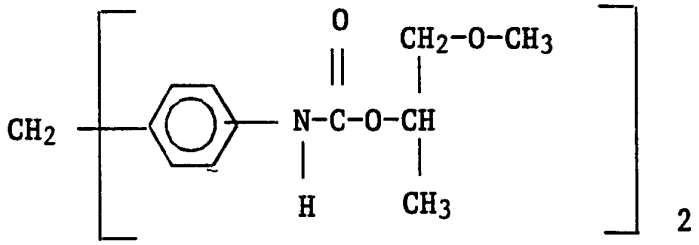
Example 2 was repeated, except that the starting biscarbamate was 62.8 parts of MDI dimethyl biscarbamate. The product contained 80.3 parts of MDI di(1-methoxy isopropanol) biscarbamate.

Example 4

Example 2 was again repeated, this time substituting 0.9 g titanium (IV) isopropoxide for the dibutyltin dilaurate. After 72 hours reaction, 79.5 parts of MDI di(1-methoxy isopropanol) biscarbamate were obtained.

Example 5

Into a distillation flask equipped with a heating mantle was charged a mixture of 18.8 g 1-methoxy-2-propanol and 43.2 g of a biscarbamate as represented by the structure (MDI di(1-methoxy isopropanol) biscarbamate):



The mixture was heated under full vacuum to a temperature of less than 100°C, and 22.6 grams of the 2-hydroxy-3-methoxypropane distilled off. This distillate was recovered in a cold trap. The material remaining in the distillation flask had a resinous appearance and appeared to include an allophanate or polyurethane formed from the biscarbamate. In a second stage, the distillation flask was then heated to a temperature of 180 to 220°C, and a mixture of isocyanates and 1-methoxy-2-propanol began to distill. The temperature of the distillate was 140 to 180°C. The isocyanates condensed separately from the 1-methoxy-2--propanol and were recovered in a condensation flask upstream of the cold trap where the 1-methoxy-2-propanol was condensed. The isocyanates distilled from this had an NCO content of 22.4 percent, representing approximately 48 percent MDI and 52 percent of the monocarbamate. The distillation was continued until the distillation flask was empty except for a tarry residue which did not further decompose or distill. This residue was recovered and found to weigh 1.6 g, which represented 4 percent of the initial mixture of biscarbamate and 2-hydroxy-3-methoxypropane.

A total of 21.3 g of a crystalline polyisocyanate containing 22 percent NCO groups was recovered. A total of 39.5 grams of 1-methoxy-2-propanol was recovered. This amount represented over 100 percent of theoretical, but upon examination it was seen that some MDI was present in the alcohol.

The isocyanates (20 g) recovered from the preceding pyrolysis were pyrolyzed a second time under the same conditions. The distillate obtained from this second pyrolysis had an NCO content of 32 percent, representing approximately 92 percent MDI and 8 percent monocarbamate. A tarry residue weighing only 0.3 g remained in the pyrolysis flask.

Examples 6-7 and Comparative Sample A

A series of MDI biscarbamates was pyrolyzed using the apparatus described in Example 5. In all cases, the pyrolysis was run under the same conditions as described in Example 5.

The weight of the starting biscarbamate, the recovered isocyanates, the recovered alcohol and tarry residue were as reported in Table 1.

TABLE 1

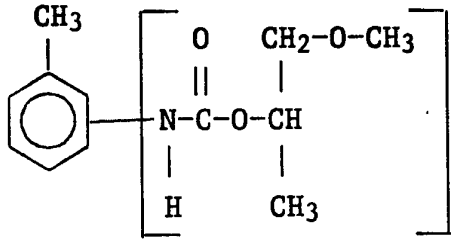
Sample No.	MDI BISCARBAMATE	WT. BISCARBAMATE, g	WT. ISOCYANATE, g	WT. ALCOHOL g	WT. TAR, g (%)①
6	Di-3,3-dimethyl-2-butyl	75.2	33.7	33.2	4.5 (5.9%)
7	Di-1-methoxy-2-propyl	27.8	13.0	13.2	0.7 (2.5%)
A*	Diethyl	30.2	5.3	10.2	13.7 (45.4%)

①Based on the weight of the MDI biscarbamate starting material.
* - Not an example of the invention.

As can be seen from the data in Table 1, the biscarbamates of this invention (Samples 6 and 7) formed minimal tar when pyrolyzed in the absence of solvent. On the other hand, almost half of the MDI diethylbiscarbamate formed a tarry residue under these conditions.

Example 8

TDI di-1-methoxy-2-propyl biscarbamate (48.4 g), having the structure



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was pyrolyzed in an apparatus similar to that described in Example 8, at 180-250°C under 1 mm Hg vacuum. A distillate was collected at 150-160°C, weighing 34.5 g and having an NCO content of 17.2 percent. In a separate dry ice trap, 12.9 g of 1-methoxy-2-propanol was

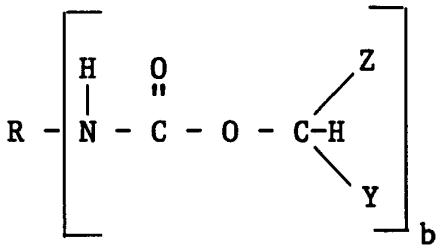
collected. The NCO content of the distillate indicated that it was predominantly the monocarbamate of TDI. The pyrolysis flask contained 0.85 g of tar, representing 1.8 percent of the weight of the starting material.

The distillate was then pyrolyzed again under the same conditions. This time, two distillates were collected--one at 75-85°C (predominantly TDI) and one at 165-175°C (predominantly the monocarbamate). The polymeric tar in the flask weighed less than 1 percent of the weight of starting material.

Example 9

H_{12}MDI di-1-methoxy-2-propyl biscarbamate (107.0 g) was pyrolyzed under the same conditions used in Example 5. The products of this pyrolysis were 41.9 g of a polyisocyanate having an NCO content of 26.6 percent, 55.1 g of 1-methoxy-2-propanol and 9.7 g tarry residue.

1. A polycarbamate as represented by the structure



wherein b is a number of two or more, R is an organic radical with a valence equal to b, Y is a group having at least two carbon atoms, and Z is an aliphatic or aromatic group containing at least one carbon atom.

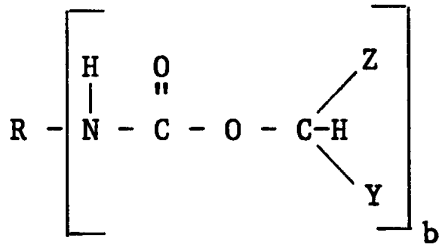
2. The polycarbamate of claim 1 wherein Z is a C_1-C_4 straight chain alkyl, C_3-C_6 branched alkyl, methoxy- or ethoxy-substituted C_1-C_4 alkyl, phenyl or benzyl group, and Y is represented by the structure $-CR^1R^2R^3$ wherein R^1 and R^2 are independently hydrogen, C_1-C_6 alkyl, aromatic, benzyl, alkoxy or phenoxy and R^3 is C_1-C_6 alkyl, aromatic, benzyl, alkoxy, phenoxy or dialkylamine.

3. The polycarbamate of claim 2 wherein R^1 and R^2 are hydrogen, and R^3 is C_1-C_4 alkoxy or phenoxy.

4. The polycarbamate of claim 3 wherein b is 2 and R is tolylene, dicyclohexylmethane or a diphenylmethane diradical.

5. The polycarbamate of claim 4 wherein R^1 is hydrogen; R^2 is methyl, ethyl or phenyl; R^3 is methoxy or ethoxy; and Z is methyl or ethyl.

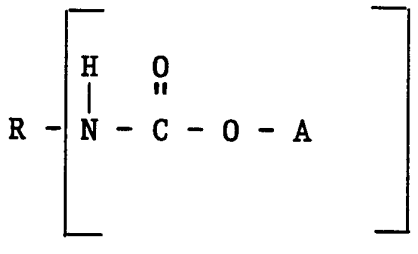
6. A process for preparing a polyisocyanate, comprising pyrolyzing a polycarbamate represented by the structure



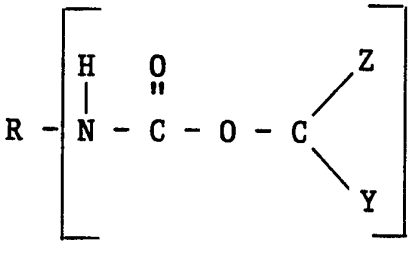
wherein b is a number of two or more, R is an organic radical with a valence equal to b, Y is a group having at least two carbon atoms, and Z is an aliphatic or aromatic group containing at least one carbon atom, under reduced pressure and at a temperature of 150 to 270°C, to form the corresponding polyisocyanate and alcohol.

7. The process of claim 6 which is conducted in the substantial absence of a solvent.

8. A process comprising reacting a first polycarbamate represented by the structure



wherein A is C_{1-6} linear alkyl, b is a number of two or more and R is an organic radical with a valence equal to b, with a secondary alcohol represented by the structure Z-CH(OH)-Y, wherein Y is a group having at least two carbon atoms, and Z is an aliphatic or aromatic group containing at least one carbon atom, at an elevated temperature such that a second polycarbamate represented by structure



and an alcohol of the structure A-OH are formed, and wherein the alcohol A-OH is removed from the product polycarbamate continuously or intermittently as it forms.

9. The process of claim 14 wherein said elevated temperature is from 100°C and 250°C, and no organometallic catalyst is present.

10 The process of claim 14 wherein Z is a C_1-C_4 straight chain alkyl, C_3-C_6 branched alkyl, methoxy- or ethoxy-substituted C_1-C_4 alkyl, phenyl or benzyl group, and Y is represented by the structure $-CR^1R^2R^3$ wherein R^1 and R^2 are independently hydrogen, C_1-C_6 alkyl, aromatic, benzyl, alkoxy or phenoxy and R^3 is C_1-C_6 alkyl, aromatic, benzyl, alkoxy, phenoxy or dialkylamine.

INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/US 95/02068

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C271/08 C07C271/28 C07C263/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 110, no. 7, 13 February 1989, Columbus, Ohio, US; abstract no. 57181, YANAGII, TOYOKAZU; ITOKAZU, TERUO 'Preparation of isophorone diisocyanate by pyrolysis of 3-alkoxycarbonylaminomethyl-3 ,5,5-trimethyl-1-alkoxycarbonylaminocycloh exanes' page 642 ; see abstract and RN 118432-50-1 & JP,A,63 162 662 (DAICEL CHEMICAL INDUSTRIES) 6 July 1988 --- -/--	1,2,6

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 June 1995	16. 06. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Seufert, G

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 120, no. 22, 30 May 1994, Columbus, Ohio, US; abstract no. 275185, L. ZIEMIANSKI ET AL 'Preparation of dicarbamate diester detergent additives for gasoline' page 282 ; see RN 149789-19-5 & PL,A,153 996 29 November 1991 ---	1,2
X	CHEMICAL ABSTRACTS, vol. 115, no. 15, 14 October 1991, Columbus, Ohio, US; abstract no. 158673, J. NOWAKOWSKI 'Derivatives of carbamic acid and urea. part IV.' page 890 ; see RN 136397-49-4 & POL. J. CHEM., vol.64, no.7-12, 1990 pages 725 - 729 ---	1,2
X	CHEMICAL ABSTRACTS, vol. 115, no. 5, 5 August 1991, Columbus, Ohio, US; abstract no. 49137g, J. NOWAKOWSKI ET AL. 'Preparation of 3,3'-benzophenonebis(alkyl carbamates) as herbicides' page 790 ; see RN 106752-81-2, 106752-74-3 & PL,A,151 341 ---	1,2
X	CHEMICAL ABSTRACTS, vol. 67, no. 15, 9 October 1967, Columbus, Ohio, US; abstract no. 73074, V. T. SINYAVSKII ET AL. 'Products of the reaction of hexamethylene diisocyanate with some alcohols' page 6863 ; see abstract and RN 16644-52-3 & ZH. ORG. KHIM., vol.3, no.5, 1967 pages 870 - 873 ---	1,2
X	JOURNAL OF ORGANIC CHEMISTRY, vol.23, 1958, EASTON US pages 906 - 907 R. G. BOSSERT 'Carbamates. I. From monohydric alcohols and toluene-2,4-diisocyanate' see table I, example 7 --- -/--	1,2

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 57, no. 9, 29 October 1962, Columbus, Ohio, US; abstract no. 11175i, PRITAM SINGH, J. L. BOIVIN 'Studies on the stability of the dimer of 2,4-tolylene diisocyanate' see abstract and RN 102380-54-1 & CAN. J. CHEM., vol.40, 1962 pages 935 - 940 ---	1,2
X	CHEMICAL ABSTRACTS, vol. 118, no. 14, 5 April 1993, Columbus, Ohio, US; abstract no. 126595, M. M. MILLER, J. S. PLOTKIN, 'Radiation-curable polypropenyl ether resins for coating materials' page 101 ; see abstract and RN 126595 & US,A,5 140 054 18 August 1992 ---	1
X	CHEMICAL ABSTRACTS, vol. 117, no. 24, 14 December 1992, Columbus, Ohio, US; abstract no. 237046, NAKAHARA, MAKOTO; IZUMI MASSAO 'Lubricating oils for refrigerator compressors' page 179 ; see RN 144252-59-5 & JP,A,04 136 095 (SANKEN KAKO CO.) 11 May 1992 ---	1
X	CHEMICAL ABSTRACTS, vol. 108, no. 22, 30 May 1988, Columbus, Ohio, US; abstract no. 187415, TAKIYAMA, EIICHIRO; TAKANO SEIICHI 'Unsaturated urethane compounds and their manufacture' page 9 ; see RN 114267-42-4 & JP,A,62 249 961 (SHOWA HIGHPOLYMER CO.) 30 October 1987 -----	1

INTERNATIONAL SEARCH REPORT

In ational application No.
PCT/US95/02068

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

The search for compounds according to claim 1 having at least two NHCOOCH2Y groups and R being an organic radical although it has been carried out completely, revealed too many answers which for economic reasons cannot be cited all in the search report.

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searches without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/

Therefore the search report shall not be considered complete for all claims. The cited documents are an arbitrary selection of retrieved answers for compound according to claim 1.
All retrieved documents for claim 1 were examined for their use in the preparation of isocyanates according to claims 6 - 10. The search report is complete for claims 3, 4, 6 - 10.

INTERNATIONAL SEARCH REPORT

..nformation on patent family members

Interr ·nal Application No
PCT/US 95/02068

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP-A-63162662	06-07-88	NONE	
PL-A-153996		NONE	
PL-A-151341		NONE	
US-A-5140054	18-08-92	NONE	
JP-A-04136095	11-05-92	NONE	
JP-A-62249961	30-10-87	JP-C- 1652538 JP-B- 3014015	30-03-92 25-02-91