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(71) Applicants: **WANHUA CHEMICAL (NINGBO) CO., LTD.** [CN/CN]; Wanhua Industrial Park, 39 Huandao Road (North), Daxie Development Zone, Ningbo, Zhejiang 315812 (CN). **WANHUA CHEMICAL GROUP CO., LTD** [CN/CN]; No.7 Xingfu South Road, Zhifu District, Yantai, Shandong 264002 (CN).

(72) Inventor: **SUN, Lidong**; Wanhua Industrial Park, 39 Huandao Road (North), Daxie Development Zone, Ningbo, Zhejiang 315812 (CN).

(74) Agent: **BOSS & YOUNG PATENT AND TRADE-MARK LAW OFFICE**; 5/F., Tower A, Bldg. No. 1, GT International Center, Jia 3 Yongandongli, Jianguomenwai Avenue, Chaoyang District, Beijing 100022 (CN).

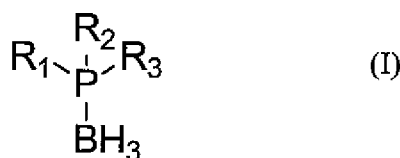
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(54) Title: PROCESS FOR PREPARING ISOCYANATE HOMOPOLYMERS CONTAINING URETDIONE GROUPS



(57) **Abstract:** The present invention relates to a process for preparing isocyanate homopolymers containing uretdione groups, in which the phosphinoboron compound of formula (I) are used as catalysts to catalyze the homopolymerization reaction of raw isocyanates, thereby obtaining a solution of isocyanate homopolymers having uretdione groups, then separating the solution and thus obtaining the isocyanate homopolymers containing uretdione groups. The isocyanate homopolymers containing uretdione groups prepared by this process have a high amount of the uretdione groups, wherein the dependence of the amount on the conversion rate of raw isocyanates is significantly ameliorated, with low chromaticities.

## PROCESS FOR PREPARING ISOCYANATE HOMOPOLYMERS CONTAINING URETDIONE GROUPS

### Field of the Invention

5        The present invention relates to a process for preparing isocyanate homopolymers with a high uretdione group content.

### Background of the Invention

10        Isocyanate homopolymers containing uretdione groups have a particularly low viscosity, thus, as crosslinkers, they have relatively good applicabilities in coating compositions with low solvent and a high solid content.

      The key in preparation of isocyanate homopolymers with a high uretdione group content is to select catalysts. Catalysts reported in patents mainly include tertiary phosphine compounds, boron trifluoride compounds, and pyridine compounds.

15        DE 1670720 discloses a process for preparing isocyanate homopolymers containing uretdione groups by using at least one aliphatically substituted tertiary phosphine or boron trifluoride compound. The isocyanate homopolymers obtained by this process have a relatively high uretdione content, however, the conversion rate thereof is low.

      The preparation of polyisocyanates containing uretdione groups are disclosed in CN 1502605 and CN 1660792, in both of which the catalysts used are tertiary phosphines containing cycloalkyl substituent or directly phosphorus-attached cycloalkyl substituent. The imperfection lies in that the content of uretdione group highly depends on the conversion rate in the preparation of isocyanate homopolymers containing uretdione groups. In another word, isocyanate homopolymers with a high uretdione group content can be only obtained under the condition of relatively low conversion rate of isocyanate. Accordingly, a large amount of unreacted raw isocyanate monomers are required to be recovered in the product separation stage, thereby rendering a high processing energy cost.

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      US 8134014 discloses a process for preparing polyisocyanates containing uretdione group, in which the catalysts used are aminopyridine compounds substituted by fused ring(s). The prepared isocyanate homopolymers have a relatively high uretdione group content, and there is no special limitation on the applicable isocyanates. However, the pyridine compounds used tend to color the products. As a result, there is still a need of developing specific processes, wherein

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the contents of uretdione groups are high with less dependence on the conversion rate of raw isocyanates, and the chromaticity of products as well as the cost of processing energy is low.

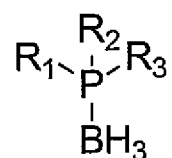
### **Summary of the Invention**

5 The object of present invention is to provide a process for preparing isocyanate homopolymers containing uretdione groups, in which the phosphinoboron compounds are used as catalysts to catalyze isocyanate homopolymerization, thereby preparing isocyanate homopolymers containing uretdione groups. The isocyanate homopolymers obtained in this process have a high uretdione group content, with an obvious ameliorated dependence on the  
10 convention rate of the raw isocyanates, and the chromaticity of products is low as well as the cost of processing energy is prominently reduced.

In order to achieve the aforementioned purposes, the present invention adopts the following technical solutions:

15 A process for preparing isocyanate homopolymers containing uretdione groups, which includes:

in the presence of catalysts, homopolymerizing at least one kind of the raw isocyanates to prepare isocyanate homopolymers containing uretdione groups, wherein the catalysts are phosphinoboron compounds with the structure of formula (I):



(I)

20 where, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are independently selected from linear or branched C<sub>1</sub>-C<sub>20</sub> alkyl group, optionally substituted C<sub>3</sub>-C<sub>20</sub> cycloalkyl group, optionally substituted C<sub>7</sub>-C<sub>15</sub> aralkyl group or optionally substituted C<sub>6</sub>-C<sub>12</sub> aryl group; and

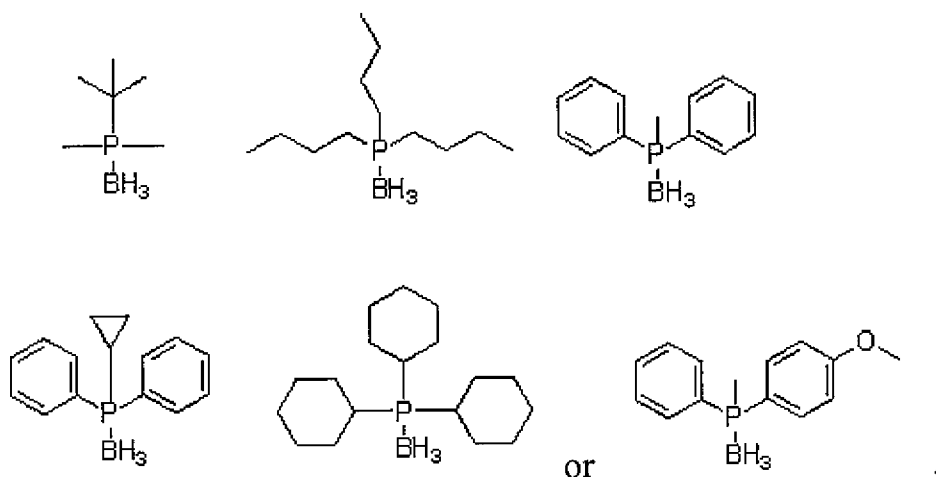
25 wherein the term "optionally substituted" refers to the group can be substituted by single or multiple substituent(s) selected from C<sub>1</sub>-C<sub>10</sub> alkyl group, C<sub>1</sub>-C<sub>10</sub> alkoxyl group, C<sub>6</sub>-C<sub>12</sub> aryl group or C<sub>7</sub>-C<sub>15</sub> aralkyl group; or unsubstituted.

30 Preferably, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are independently selected from methyl, linear or branched C<sub>3</sub>-C<sub>20</sub> alkyl group, alkyl-substituted C<sub>3</sub>-C<sub>20</sub> cycloalkyl group, alkyl-substituted C<sub>7</sub>-C<sub>15</sub> aralkyl group, alkyl-substituted C<sub>6</sub>-C<sub>12</sub> aryl group or alkoxyl-substituted C<sub>6</sub>-C<sub>12</sub> aryl group; wherein, the alkyl substituents are selected from C<sub>1</sub>-C<sub>10</sub> linear or branched alkyl group, and the alkoxyl substituents

are selected from C<sub>1</sub>-C<sub>10</sub> alkoxyl group.

More preferably, R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are independently selected from methyl, n-butyl, tert-butyl, cyclopropyl, cyclohexyl, phenyl or methoxyphenyl.

The phosphinoboron compound catalysts of formula (I) in the present invention are preferably selected from one, two or more of the following catalysts:



The raw isocyanate monomer of the present invention is selected from one of the following compounds: aliphatic isocyanate, cycloaliphatic isocyanate or aromatic isocyanate; wherein the isocyanate having a NCO functionality  $\geq 2$ .

For instance, the raw isocyanate monomers of the present invention are preferably selected from one of the following compounds: tetramethylene-1,4-diisocyanate, pentamethylene-1,5-diisocyanate, hexamethylene-1,6-diisocyanate, lysine diisocyanate, isophorone diisocyanate, trimethylhexamethylene diisocyanate, dicyclohexylmethane diisocyanate, norbornane dimethylene isocyanate, diphenylmethane diisocyanate, toluene diisocyanate or p-phenyl diisocyanate. More preferably, they are selected from hexamethylene-1,6-diisocyanate or isophorone diisocyanate.

The amount of phosphinoboron compound catalyst in accordance with formula (I) used in the present invention is 0.1-4 mol% of the amount of raw isocyanate monomer, preferably is 0.5-2 mol%, based on the mole amount of raw isocyanate monomers.

The phosphinoboron compound catalysts of formula (I) in the present invention can be used solely or as a formulated solution, wherein the concentration of the formulated solution is 0.5-5 mol/L, preferably 2-4 mol/L; and the solvents used in formulating the solution are free of the active hydrogen; preferably, one, two or more of halogenated hydrocarbons, aromatic

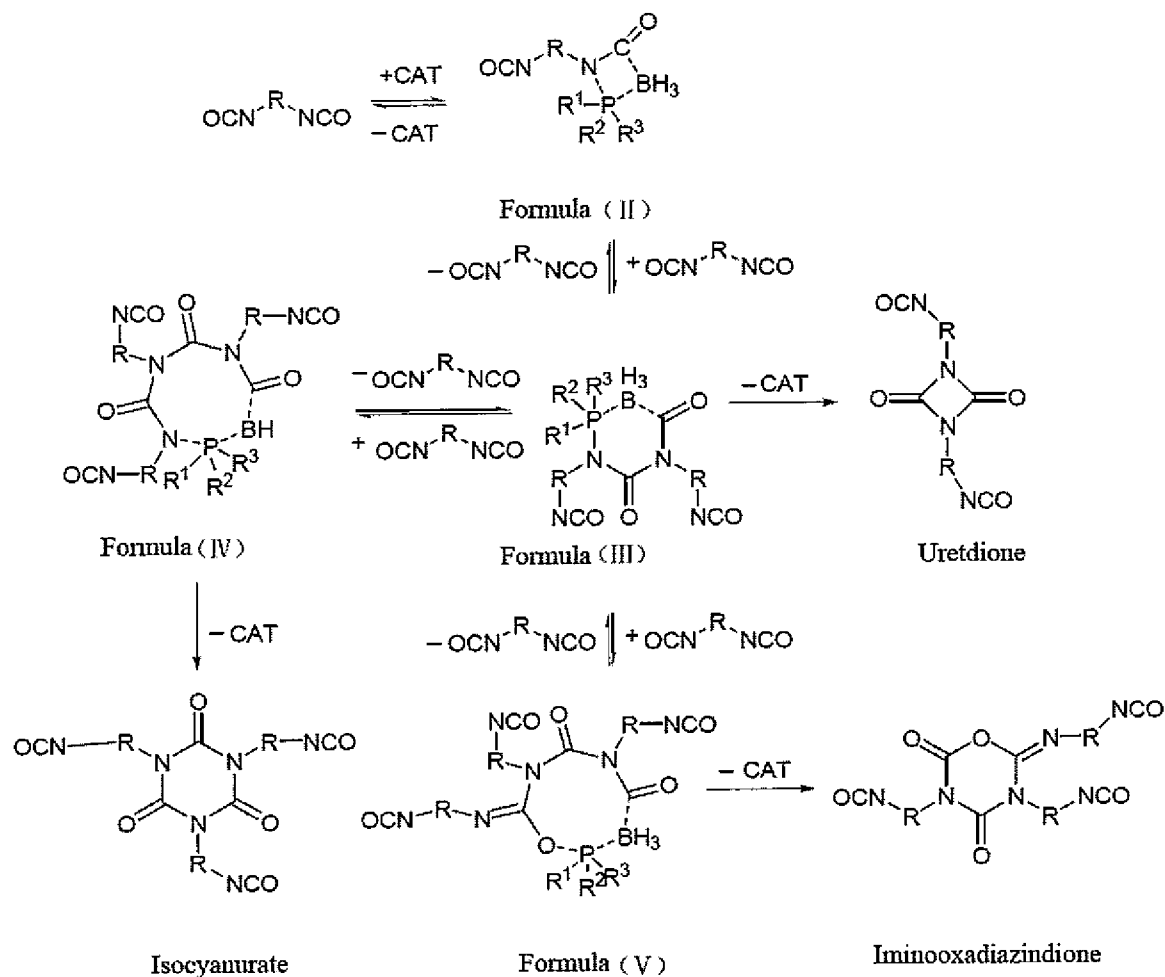
hydrocarbons or ethers; more preferably, one, two or more of dichloromethane, tetrahydrofuran, methylbenzene, dimethylbenzene or chlorobenzene.

In the present invention, the temperature of the homopolymerization reaction of the raw isocyanate monomers is 20-120 °C, preferably, 50-100 °C.

5 In the process of the present invention, when the conversion rate of isocyanates reaches 20%-60% (based on the mass of raw isocyanate monomers), the homopolymerization reaction is terminated by using catalyst poisons. The catalyst poisons can be the known alkylating agents including dimethyl sulphate, methyl p-toluenesulphonate etc.; or phosphate esters including dimethyl phosphate, diethyl phosphate, di-n-butyl phosphate and so on. The mole ratio of the  
10 catalyst poison to the catalyst is 1:1-2:1; preferably 1:1-1.2:1.

At a suitable temperature, the phosphinoboron compound catalysts of formula (I) according to the present invention with a molecule of isocyanate can firstly form a transition state of four-membered ring structure having the structure of formula II, and further activate the carbon atom of NCO function group in the raw isocyanates, thereby rendering more liable to bond with  
15 another molecule of isocyanate, and can further result in a transition state as a six-membered ring structure of formula III. Since the transition state of the six-membered ring is relatively stable, its ratio is higher than every other intermediate transition state during the polymerization process of isocyanates (during the polymerization process, there are transition states of nine-membered rings for forming isocyanurate and iminooxadiazindione, i.e. formulae IV and V), it is the primary  
20 intermediate transition state. Accordingly, after the catalysts of the transition states of formulae III, IV and V are removed, the uretdione, isocyanurate and iminooxadiazindione are obtained, respectively, wherein the uretdione accounts for the main part.

In order to illustrate clearly, the homopolymerization process is described in the following formulae, wherein OCN-R-NCO denotes the raw isocyanate monomer, CAT represents the  
25 catalysts with the structure of formula (I).



According to the process of the present invention, using the phosphinoboron compounds of the present invention as catalysts can effectively catalyze the homopolymerization reaction of raw isocyanate monomers to prepare polyisocyanates with a high uretdione group content. Compared with the preparation processes by using the catalysts in the art, the process of the present invention achieves a higher conversion rate of raw isocyanates as well as a higher uretdione content in the product. Meanwhile, lower chromaticity can be obtained via preparing the polyisocyanates by using phosphinoboron compounds of formula (I) according to the present invention as catalysts.

### Detailed Description of the Preferred Embodiments

The process provided by the present invention would be further illustrated by the following embodiments, but the present invention is not limited to these embodiments.

Gel chromatography (LC-20AD/RID-10A, columns: MZ-Gel SDplus 10E3A 5  $\mu\text{m}$  (8.0 $\times$ 300mm), MZ-Gel SDplus 500A 5  $\mu\text{m}$  (8.0 $\times$ 300mm), MZ-Gel SDplus 100A 5  $\mu\text{m}$  (8.0 $\times$ 300mm) in series, Shimadzu; mobile phase: tetrahydrofuran; flow rate: 1.0 mL/min;

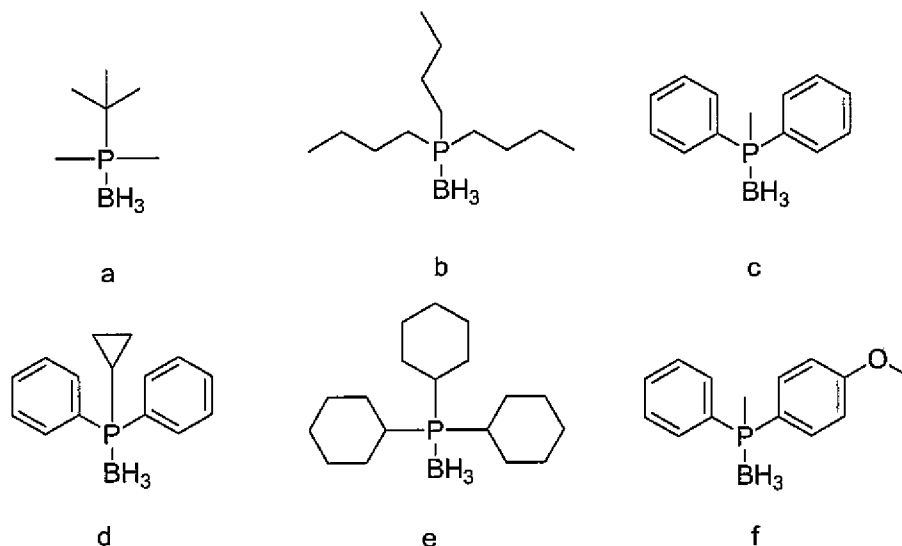
retention time: 40 min, column temperature: 35 °C) is applied to quantify the isocyanate monomers, which is used as a monitoring manner to determine the reaction conversion rate (based on the mass of raw isocyanate monomers).

The mole ratio of uretdione-containing polymers to the sum of other polymer components (i.e. the sum of polyisocyanates and polyiminooxadiazindione) in the resulted polyisocyanate homopolymers in the examples and the comparative examples is denoted as U/O. The measurement of U/O value referenced to the method described in CN101289427, wherein the  $^{13}\text{C}$ -NMR is applied. The instrument used is Bruker 400MHz, the concentration of sample is 50% ( $\text{CDCl}_3$  solution), testing condition is 100 MHz, relaxation time: 4 sec, 2000 scans/min,  $\delta=77.0\text{ppm}$  of  $\text{CDCl}_3$  is taken as the reference of chemical shift.

BYK LCS III is chosen as a colorimeter, with 50 mm sample cell, pure water (0 Hazen) is used as a reference.

All reactant solutions are under an atmosphere of dry nitrogen before the reaction starts to the addition of catalysts and during the whole reaction process, unless specifically noted otherwise.

Catalysts involved in the examples of the present invention are selected from:



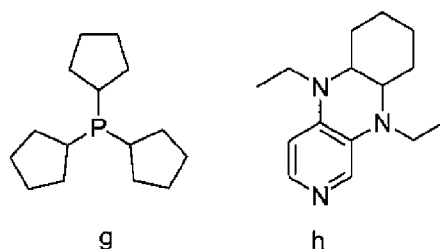
Wherein catalyst **a** was purchased from Sigma-Aldrich; catalyst **b** was prepared according to the process of the reference (Tetrahedron, 2009, 65, 6410-6415); catalyst **c**, **d** and **f** were prepared in accordance with the method described in the reference (J. Am. Chem. Soc, 1990, 112, 5244-5252); catalyst **e** was prepared according to the process of the reference (Tetrahedron, 2009, 65, 6410-6415).

For example, the process for preparing catalyst **b** was as follows:

- 1) At room temperature, 100 ml  $\text{CH}_2\text{Cl}_2$  and 10 mmol tertiary phosphine were added into a 250 mL three necked flask under the nitrogen atmosphere, and the reactants were started to stir;

- 2) The reaction was stirred for 10 min before adding 100ml  $\text{BH}_3\text{SMe}_2$  solution (1mol/L in  $\text{SMe}_2$ ), then stirred for 24 h at room temperature;
- 3) 50 ml saturated ammonium chloride solution was added in the flask, after stirring for 10 min, all of the solution in the flask was poured into a separatory funnel containing 100 ml pure water, and extracted with  $\text{CH}_2\text{Cl}_2$  for three times. The organic phase was washed with saturated sodium bicarbonate solution, and dried with dry magnesium sulfate for 24 h;
- 4) The solution was vacuum filtrated to remove the solid magnesium sulfate after dryness, then the filtrate was concentrated with a rotary evaporator;
- 5) After concentrating, the solution was separated and purified by silica-gel column chromatography using  $\text{CH}_2\text{Cl}_2$  as a eluent;
- 6) The resulted 7 mmol solid catalyst **b** was formulated into an 0.5 mol/L of  $\text{CH}_2\text{Cl}_2$  solution for use.

The catalysts in the comparative examples were selected from **g** and **h** with the following structures reported in the patent documents, i.e. CN 1502605 and CN 101450928, respectively:



### Examples 1-6

The general experimental steps of examples 1-6 are as follows:

To a four-necked flask containing 1680g (10 mol) hexamethylene-1,6-diisocyanate (HDI) at 55 °C was added a certain amount of catalysts with stirring, and timing was started. During the reaction, the temperature was maintained between 55 °C and 65 °C, the HDI was quantified by the gel chromatography to monitor the conversion rate of reaction. Once the required conversion rate was achieved, a certain amount of terminating agent was added to cease the reaction. After the reaction was finished, separation was conducted and a light colored HDI homopolymer with a high uretdione content was obtained. Detail conditions are listed in table 1.

Table 1 Experimental Conditions of Examples 1-6

	Catalyst	Catalyst Amount (based on the amount of HDI, mol%)	Using Condition	Solution and Concentration (mol/L)	Terminating Agent	Amount of Terminating Agent (mol)
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Example 1	a	0.1	Solid	-	diethyl phosphate	0.01
Example 2	b	0.5	Solution	5 (dichloromethane)		0.05
Example 3	c	1	Solution	4 (dichloromethane)		0.12
Example 4	d	2	Solution	2 (tetrahydrofuran)		0.24
Example 5	e	2	Solid	-		0.20
Example 6	f	3	Solution	0.5 (tetrahydrofuran)		0.30

### Comparative example 1

Referring to the process of CN 1502605, the process is similar to example 1, except using 0.12 mol catalyst **g** in catalyzing the homopolymerization reaction and 0.14 mol diethyl phosphate in terminating the reaction.

### Comparative example 2

Referring to the process of CN 101450928, the process is similar to example 1, except using 0.24 mol catalyst **h** in catalyzing the homopolymerization reaction and 0.24 mol diethyl phosphate in terminating the reaction.

Table 2 U/O Values of the HDI Homopolymers Prepared in Examples 1-6 and Comparative Examples 1-2

U/O Conversion Rate	U/O Values of the Prepared HDI Homopolymers							
	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2
20%	53.1	52.2	54.6	55.6	57.1	55.4	32.6	47.2
30%	42.3	41.4	43.5	44.6	46.8	43.5	12.3	33.3
45%	31.7	31.2	33.5	35.1	37.7	33.4	7.8	20.6
60%	20.3	20.1	22.7	23.0	24.5	22.3	4.4	9.1

All content ratios of uretdione to other polymer components (U/O values) in the HDI homopolymers prepared by the catalysts (examples 1-6) of the present invention are totally higher than those of the comparative examples; furthermore, as the conversion rate increases

from 20% to 60%, the decrease of U/O value is obviously smaller than those in the comparative examples.

Table 3 Chromaticity of the HDI Homopolymers Prepared in Examples 1-6 and Comparative

Examples 1-2

Chromaticity Conversion Rate	Chromaticity of the Prepared HDI Homopolymers (Hazen)							
	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1	Comparative Example 2
20%	26	27	24	22	21	23	32	37
30%	29	31	27	24	24	25	35	45
45%	32	34	31	29	27	31	38	49
60%	36	37	35	32	31	33	43	57

Chromaticities of the homopolymers prepared by the catalysts (examples 1-6) of the present invention are obviously lower than those of the comparative examples; furthermore, as the conversion rate increases from 20% to 60%, the increase of chromaticity in examples is obviously smaller than those in the comparative examples.

Examples 7-12

The general experimental steps of examples 7-12 are as follows:

To a four-necked flask containing 2222g (10 mol) isophorone diisocyanate (IPDI) at 70 °C was added a certain amount of catalysts with stirring, and timing was started. During the reaction, the temperature was maintained between 70 °C and 100 °C, the IPDI was quantified by the gel chromatography to monitor the conversion rate of reaction. Once the required conversion rate was achieved, a certain amount of terminating agent was added to cease the reaction. After the reaction was finished, separation was conducted and a light colored IPDI homopolymer with a high uretdione content was obtained. Detail conditions are listed in table 4.

Table 4 Experimental Conditions of Examples 7-12

Catalyst	Catalyst Amount (based on the amount of IPDI, mol%)	Using Condition	Solution and Concentration (mol/L)	Terminating Agent	Amount of Terminating Agent (mol)
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Example 7	a	0.5	Solid	-	diethyl phosphate	0.06
Example 8	b	1	Solution	5 (dichloromethane)		0.12
Example 9	c	2	Solution	4 (dichloromethane)		0.24
Example 10	d	2	Solution	2 (tetrahydrofuran)		0.24
Example 11	e	3	Solid	-		0.30
Example 12	f	4	Solution	0.5 (tetrahydrofuran)		0.40

### Comparative example 3

Referring to the process of CN 101450928, the process is similar to example 7, except using 0.35 mol catalyst **h** in catalyzing the homopolymerization reaction and 0.35 mol dimethyl phosphate in terminating the reaction..

Table 5 U/O Values of the IPDI Homopolymers Prepared in Examples 7-12 and Comparative Examples 3

U/O Conversion rate	U/O Values of the Prepared IPDI Homopolymers						
	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Comparative Example 3
20%	92.4	91.8	94.2	98.1	98.8	95.6	87.8
30%	82.8	80.6	82.6	88.5	89.2	87.1	76.1
45%	64.7	61.5	63.1	69.7	70.1	66.9	55.1
60%	52.5	51.9	54.7	59.1	61.7	57.3	48.6

Table 6 Chromaticity of the IPDI Homopolymers Prepared in Examples 7-12 and Comparative Example 3

Chromaticity Conversion Rate	Chromaticity of the Prepared IPDI Homopolymers (Hazen)						
	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Comparative Example 3
20%	20	21	20	20	19	21	26
30%	22	23	22	22	21	22	28
45%	24	25	24	23	23	24	30
60%	26	28	26	25	24	26	33

### Example 13

0.01 mol Catalyst **a** and 0.1 mol catalyst **e** were added into 25 ml dichloromethane, after totally dissolved, prepare a mixed-catalyst-solution **m** for later use. 1680 g (10 mol) Hexamethylene-1,6-diisocyanate (HDI) was placed in a four-necked flask at 60 °C with stirring, and timing was started. During the reaction, the temperature was maintained between 60 °C to 67 °C, the HDI was quantified with gel chromatography to monitor the conversion rate of reaction. Once the required conversion was achieved, 0.12 mol diethyl phosphate was added to terminate the reaction. After the reaction was finished, separation was conducted and a light colored HDI homopolymer with a high uretdione content was obtained.

Table 7 U/O Values and Product's Chromaticity of the HDI Homopolymers Prepared in Example 13

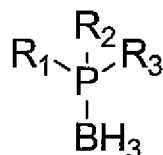
Conversion Rate of HDI	U/O Value	Product's Chromaticity/Hazen
20%	56.1	22
30%	45.8	25
45%	36.5	28
60%	23.9	32

When a combination of several catalysts of the present invention was applied, the prepared HDI homopolymer have a lower chromaticity; and the increase of chromaticity is obviously smaller when the conversion rate increases from 20% to 60%.

### Claims

1. A process for preparing isocyanate homopolymers containing uretdione groups comprising:

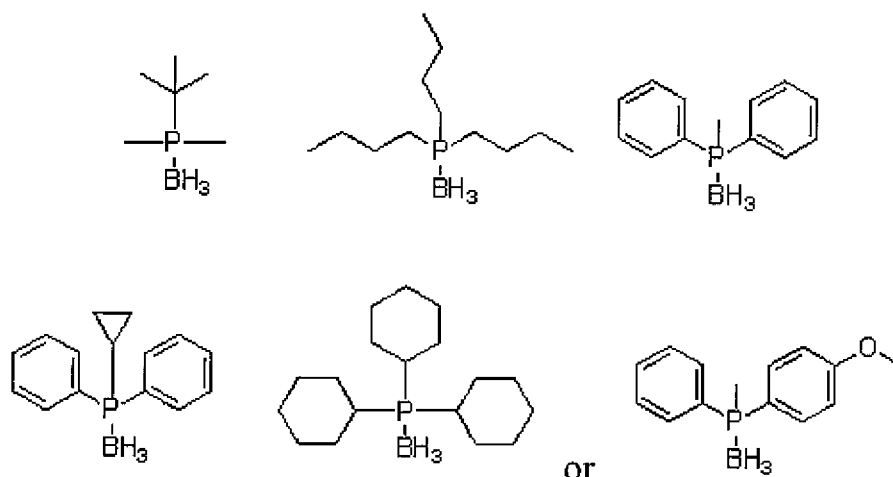
in the presence of catalysts, homopolymerizing the raw isocyanate monomers to prepare isocyanate homopolymers containing uretdione groups, wherein the catalysts are phosphinoboron compounds of the structure of formula (I):



(I)

wherein  $R_1$ ,  $R_2$  and  $R_3$  are independently selected from linear or branched  $C_1$ - $C_{20}$  alkyl group, optionally substituted  $C_3$ - $C_{20}$  cycloalkyl group, optionally substituted  $C_7$ - $C_{15}$  aralkyl or optionally substituted  $C_6$ - $C_{12}$  aryl group; preferably,  $R_1$ ,  $R_2$  and  $R_3$  are independently selected from methyl, linear or branched  $C_3$ - $C_{20}$  alkyl, alkyl-substituted  $C_3$ - $C_{20}$  cycloalkyl group, alkyl-substituted  $C_7$ - $C_{15}$  aralkyl group, alkyl-substituted  $C_6$ - $C_{12}$  aryl group or alkoxy-substituted  $C_6$ - $C_{12}$  aryl group; more preferably,  $R_1$ ,  $R_2$  and  $R_3$  are independently selected from methyl, n-butyl, tert-butyl, cyclopropyl, cyclohexyl, phenyl or methoxyphenyl.

2. The process according to claim 1, wherein the phosphinoboron compound catalysts of formula (I) are one, two or more selected from the following catalysts:



3. The process according to claim 1 or 2, wherein the raw isocyanate monomer is selected from one of the following compounds: aliphatic isocyanate, cycloaliphatic isocyanate or aromatic

isocyanate; wherein the isocyanate having a NCO functionality  $\geq 2$ .

4. The process according to claim 3, wherein the isocyanates are selected from the following compounds: tetramethylene-1,4-diisocyanate, pentamethylene-1,5-diisocyanate, hexamethylene-1,6-diisocyanate, lysine diisocyanate, isophorone diisocyanate, trimethylhexamethylene diisocyanate, dicyclohexylmethane diisocyanate, norbornane dimethylene isocyanate, diphenylmethane diisocyanate, toluene diisocyanate or p-phenyl diisocyanate; preferably, the isocyanate is selected from hexamethylene-1,6-diisocyanate or isophorone diisocyanate.

5. The process according to claim 1, wherein the amount of phosphinoboron compound catalysts of formula (I) is 0.1-4 mol%, preferably 0.5-2 mol%, based on the amount of raw isocyanate monomers.

6. The process according to claim 1 or 5, wherein the phosphinoboron compound catalysts of formula (I) are used solely or as a formulated solution, wherein the concentration of the solution is 0.5-5 mol/L, preferably, 2-4 mol/L.

7. The process according to claim 6, wherein the solvents used in formulating the solution from the phosphinoboron compound catalysts are free of the active hydrogen, preferably one, two or more of halogenated hydrocarbons, aromatic hydrocarbons or ethers; more preferably one, two or more of dichloromethane, tetrahydrofuran, methylbenzene, dimethylbenzene or chlorobenzene.

8. The process according to claim 1, wherein the temperature of homopolymerization reaction is 20-120 °C; preferably, 50-100 °C.

9. The process according to claim 1, wherein, when the conversion rate of homopolymerization reaction reaches 20% - 60% based on the mass of raw isocyanate monomers, catalyst poisons are used to terminate the homopolymerization reaction.

10. The process according to claim 9, wherein the catalyst poisons are alkylating agents or phosphate esters, where a mole ratio of the catalyst poison to the phosphinoboron compound catalyst is 1:1-2:1; preferably, 1:1-1.2:1.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/072798

**A. CLASSIFICATION OF SUBJECT MATTER**

C07D 229/00(2006.01)i; C07D 251/30(2006.01)i; C07D 273/04(2006.01)i

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)

C07D229; C07D251; C07D273

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 practicable, search terms used)

CPRSABS,CNTXT,CNKI,WPI,EPODOC: +isocyanat+, phosphine 1 w borane,uret?dione, uret?dion, cataly+, phosphine, borane, boron, borone, phosphinoboron

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 103613540 A (WANHUA CHEM NINGBO CO LTD) 05 March 2014 (2014-03-05) claims 1-10	1-10
A	CN 102942525 A (YANTAI WANHUA POLYURETHANES CO LTD ET AL.) 27 February 2013 (2013-02-27) the whole document	1-10
A	CN 1660792 A (BAYER MATERIALSCIENCE AG) 31 August 2005 (2005-08-31) the whole document	1-10
A	CN 1502605 A (BAYER AG ET AL.) 09 June 2004 (2004-06-09) the whole document	1-10
A	CN 101450928 A (BAYER MATERIALS TECHNOLOGY AG ET AL.) 10 June 2009 (2009-06-10) the whole document	1-10
A	CN 101747377 A (NIPPON CHEM IND ET AL.) 23 June 2010 (2010-06-23) the whole document	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

“A”	document defining the general state of the art which is not considered to be of particular relevance	“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
“E”	earlier application or patent but published on or after the international filing date	“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
“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)	“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
“O”	document referring to an oral disclosure, use, exhibition or other means	“&”	document member of the same patent family
“P”	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

13 August 2014

Date of mailing of the international search report

20 August 2014

Name and mailing address of the ISA/

STATE INTELLECTUAL PROPERTY OFFICE OF THE  
P.R.CHINA(ISA/CN)  
6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing  
100088 China

Authorized officer

CHEN,Hui

Facsimile No. (86-10)62019451

Telephone No. (86-10)62084415

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/072798

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011126045 A1 (NIPPON CHEMICAL IND) 13 October 2011 (2011-10-13) the whole document	1-10



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

**PCT/CN2014/072798**

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	103613540	A	05 March 2014	Non e			
CN	102942525	A	27 February 2013	Non e			
CN	1660792	A	31 August 2005	CN	1660792	B	26 May 2010
				EP	1533301	B1	26 August 2009
				MX	PA04011480	A	01 July 2005
				CA	2488071	C	15 November 2011
				US	7151151	B2	19 December 2006
				JP	4848127	B2	28 December 2011
				US	2005113551	A1	26 May 2005
				DE	10354544	A1	23 June 2005
				JP	2005154443	A	16 June 2005
				ES	2330216	T3	07 December 2009
				EP	1533301	A2	25 May 2005
				CA	2488071	A1	21 May 2005
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				AT	440822	T	15 September 2009
				EP	1533301	A3	28 September 2005
CN	1502605	A	09 June 2004	CA	2450453	C	25 January 2011
				EP	1422223	B1	14 October 2009
				JP	4651932	B2	16 March 2011
				CA	2450453	A1	25 May 2004
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				US	7067654	B2	27 June 2006
				DE	10254878	A1	03 June 2004
				BR	0305203	A	31 August 2004
				US	2004106789	A1	03 June 2004
				JP	2004175803	A	24 June 2004
CN	101450928	A	10 June 2009	EP	2067773	A2	10 June 2009
				US	2009143558	A1	04 June 2009
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				DE	102007058487	A1	10 June 2009
				AT	486854	T	15 November 2010
				CN	101450928	B	29 January 2014
				BR	PI0805234	A2	28 July 2009
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				ES	2355005	T3	22 March 2011
				US	8134014	B2	13 March 2012
				JP	2009137961	A	25 June 2009
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				JP	2010138136	A	24 June 2010
				GB	0921703	D0	27 January 2010
				JP	5350767	B2	27 November 2013
				CN	101747377	B	02 April 2014
				US	2010152489	A1	17 June 2010

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/CN2014/072798**

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				US	8338391	B2	25 December 2012
WO	2011126045	A1	13 October 2011	JP	2011219413	A	04 November 2011
				JP	5465584	B2	09 April 2014