(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 May 2009 (14.05.2009)

PCT

(10) International Publication Number
WO 2009/061020 A1

(51) International Patent Classification:
D01F 6/70 (2006.01)

(21) International Application Number:
PCT/KR2007/006488

(22) International Filing Date:
13 December 2007 (13.12.2007)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
10-2007-0112524
6 November 2007 (06.11.2007) KR

(71) Applicant *(for all designated States except US)*: **HYOSUNG CORPORATION** [KR/KR]; 450, Kong-duk-dong, Mapo-gu, Seoul 121-020 (KR).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **CHOI, Mi Young** [KR/KR]; 101-206, Dongsin Apartment, Hawolgok-dong, Seongbuk-gu, Seoul 136-130 (KR). **JIN, Joong Seong** [KR/KR]; 101-910, Woosung Apartment, Samcheon-dong 1-ga, Wansan-gu, Jeonju-si, Jeollabuk-do 560-291 (KR). **KANG, Yeon Soo** [KR/KR]; 105-108, Woosung Apartment, 85, Bakdal-dong, Manan-gu, Anyang-si, Gyeonggi-do 430-030 (KR).

(74) Agents: **KIM, Hak Je** et al.; Phoenix International Patent and Law Office, Kwanghwamoon P.O. Box 1828, Seoul 110-618 (KR).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

WO 2009/061020 A1

(54) Title: METHOD FOR PREPARING POLYURETHANEUREA ELASTIC FIBER WITH IMPROVED HEAT SETTABILITY AND POLYURETHANEUREA ELASTIC FIBER PREPARED BY THE SAME

(57) Abstract: The present invention relates to a method for preparing polyurethaneurea elastic fiber, the method comprising reacting a mixture of at least one diisocyanate comprising 4,4'-diphenylmethanediisocyanate and 7 to 25 mole % of 2,4'-diphenylmethanediisocyanate with polyol to produce a prepolymer, and polyurethaneurea elastic fiber prepared by the same. The polyurethaneurea elastic fiber of the present invention has superior spinning workability, improved yarn evenness, and high heat-set efficiency even at low temperature.

Description

METHOD FOR PREPARING POLYURETHANEUREA ELASTIC FIBER WITH IMPROVED HEAT SETTABILITY AND POLYURETHANEUREA ELASTIC FIBER PREPARED BY THE SAME

Technical Field

[1] The present invention relates to a method for preparing polyurethaneurea elastic fiber with improved heat-set efficiency and polyurethaneurea elastic fiber prepared by the same, and more particularly to a method for preparing polyurethaneurea elastic fiber with improved heat-set efficiency, in which a prepolymer is prepared from a mixture of at least one of diisocyanate of polyurethaneurea comprising 4,4'-diphenylmethanediisocyanate and 2,4'-diphenylmethanediisocyanate, and polyurethaneurea elastic fiber prepared by the same.

Background Art

[2] In general, polyurethaneurea elastic fiber is prepared as follows. First, a polyol compound with a large molecular weight is reacted with excessive amount of di-isocyanate to prepare a prepolymer having isocyanate groups at both ends of the polyol. Then, after dissolving the prepolymer in an adequate solvent, a diamine- or diol-based chain extender and a chain terminator such as monoalcohol, monoamine, etc. are added to the resulting solution to produce a polyurethaneurea spinning solution. Subsequently, polyurethaneurea elastic fiber is prepared by dry- or wet-spinning the polyurethaneurea spinning solution.

[3] Such prepared polyurethaneurea fiber is characterized by its high elasticity, and widely used in a variety of areas such as functional underwear, sports wear, and the like as weaved together with polyamide, polyester or natural fibers. As its usage has expanded, there is a growing demand for developing extra features of conventional fibers.

[4] In general, polyurethaneurea fiber is heat-set at high temperature. As a result, there is thermal degradation of heat-sensitive fibers such as nylon, cotton, silk, wool, etc. that is weaved together with polyurethaneurea during post-process after knitting. In order to prevent such thermal degradation and improve dimensional stability of the fabric, it is increasingly necessary to develop a polyurethaneurea fiber to be heat-set at low temperature.

[5] Japanese Patent Laid-Open No. Hei 7-82608 discloses a method for preparing polyurethaneurea elastic fiber having excellent stability of polymer solution, not

causing knitting unevenness in processing by using diphenylmethanediisocyanate comprising 1.8 to 13 wt% fraction of 2,4'-diphenylmethanediisocyanate. The invention provides high strength at break and heat resistance, but insufficient heat-set efficiency. U.S. Patent No. 6,472,494 discloses spandex prepared from a mixture of 23 to 55 mole % of 2,4'-diphenylmethanediisocyanate and 4,4'-diphenylmethanediisocyanate, polyether glycol and a chain extender. By significantly increasing the content of the 2,4'-diphenylmethanediisocyanate to 23 to 55 mole %, the resultant polyurethaneurea elastic fiber has improved heat-set efficiency. However, it is unfavorable in spinning, because of greatly deteriorated modulus and elasticity recovery and insufficient yarn evenness.

Disclosure of Invention

Technical Problem

[6] Therefore, the present invention has been made in an effort to solve the above-described problems associated with the prior art, and it is an object of the present invention to provide a method for preparing polyurethaneurea elastic fiber with improved yarn evenness and high heat-set efficiency.

[7] It is an another object of the present invention to provide polyurethaneurea elastic fiber which is prepared by the method of the present invention and has superior spinning workability, improved yarn evenness, and high heat-set efficiency at low temperature.

Technical Solution

[8] In accordance with an aspect of the present invention, there is provided a method for preparing polyurethaneurea elastic fiber by polymerizing polyol with excessive amount of diisocyanate to produce a prepolymer (first polymerization), and dissolving the prepolymer in an organic solvent and then adding a chain extender and a chain terminator thereto (second polymerization) to produce polyurethaneurea elastic fiber, characterized in that the prepolymer is prepared by reacting a mixture of at least one diisocyanate comprising 4,4'-diphenylmethanediisocyanate and 7 to 25 mole % of 2,4'-diphenylmethanediisocyanate with polyol. Preferably, the diisocyanate is at least one selected from the group consisting of 4,4'-diphenylmethanediisocyanate, 1,5'-naphthalenediisocyanate, 1,4'-phenylenediisocyanate, hexamethylenediisocyanate, 1,4'-cyclohexanediisocyanate, 4,4'-dicyclohexylmethanediisocyanate and isophoronediisocyanate, the polyol of the prepolymer is one selected from the group consisting of polytetramethylene ether glycol, polypropylene glycol, polycarbonate diol and a combination thereof, and the chain extender is at least one selected from the group consisting of ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 2,3-diaminobutane, 1,5-diaminopentane,

1,6-hexamethylenediamine, 1,4-cyclohexanediamine and a combination thereof. Also, preferably, weight proportion of isocyanate of the prepolymer is from 1.75 % to 4.13 %.

[9] According to another aspect of the present invention, there is provide polyurethaneurea elastic fiber prepared by the method described above, which has superior spinning workability, improved yarn evenness, and high heat-set efficiency at low temperature.

Advantageous Effects

[10] According to the present invention, it is possible to produce polyurethaneurea elastic fiber with superior spinning workability, improved yarn evenness, and high heat-set efficiency. Since heat-setting can be performed at low temperature, thermal degradation of the fiber that is weaved together with polyurethaneurea can be prevented, hand-feel of the fabric can be improved, and selvage curling of knitted fabric during processing after heat-setting can be prevented.

Mode for the Invention

[11] Hereinafter, a method for preparing polyurethaneurea elastic fiber according to the present invention will be described in detail.

[12] Segmented polyurethaneurea used to prepare the elastic fiber of the present invention is prepared by reacting organic diisocyanate with polymer diol to produce a p repolymer, and dissolving the prepolymer in an organic solvent and then reacting with diamine and monoamine.

[13] Examples of the diisocyanate used to prepare the polyurethaneurea elastic fiber of the present invention may include at least one selected from the group consisting of 4,4'-diphenylmethanediisocyanate, 2,4'-diphenylmethanediisocyanate, 1,5'-naphthalenediisocyanate, 1,4'-phenylenediisocyanate, hexamethylenediisocyanate, 1,4'-cyclohexanediisocyanate, 4,4'-dicyclohexylmethanediisocyanate and isophoronediisocyanate, but is not necessarily limited thereto.

[14] In the method of the present invention, at least one diisocyanate comprising 4,4'-diphenylmethanediisocyanate is mixed with 2,4'-diphenylmethanediisocyanate. It is preferable that the proportion of the 2,4'-diphenylmethanediisocyanate is from 7 to 25 mole %. When the 2,4'-diphenylmethanediisocyanate is included in an amount less than 7 mole %, selvage curling may occur during heat-setting process at low temperature because of insufficient heat-setting efficiency. And, when it is included in an amount exceeding 25 mole %, modulus may decrease abruptly. Hence, it is preferable that the 2,4'-diphenylmethanediisocyanate is included in an amount within the aforesaid range.

[15] The polyol used in the present invention may be one selected from the group

consisting of polytetramethylene ether glycol, polypropylene glycol, polycarbonate diol and a combination thereof, but is not necessarily limited thereto.

[16] The chain extender used in the present invention may be a diamine. For example, the chain extender may be at least one selected from the group consisting of ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 2,3-diaminobutane, 1,5-diaminopentane, 1,6-hexamethylenediamine, 1,4-cyclohexanediamine and a combination thereof, but is not necessarily limited thereto.

[17] Examples of the chain terminator used to control the molecular weight of polyurethaneurea may include amine having one functional group such as di-ethylamine, monoethanolamine, dimethylamine and so on.

[18] Furthermore, in order to prevent discoloration or property impairment of polyurethaneurea that may be caused by UV, smog or heat-setting process for spandex, sterically hindered phenolic compounds, benzofuranone based compounds, semi-carbazide based compounds, benzotriazole based compounds, or polymeric tertiary amine stabilizers may be added in combination into a spinning solution.

[19] In addition, the polyurethaneurea elastic fiber of the present invention may further comprise additives such as titanium dioxide, magnesium stearate, etc.

[20] Preferably, the weight proportion of isocyanate of the prepolymer is maintained from 1.75 % to 4.13 % so as to have the properties of polyurethaneurea elastic fiber.

[21]

[22] Hereinafter, the present invention will be described in detail with reference to the following non-limiting examples. It should nevertheless be understood that the same is considered as illustrative and no limitation of the scope of the present invention is thereby intended.

[23]

[24] In the following Examples and Comparative Examples, heat-set efficiency, NCO%, U%, workability, selvage curling and hand-feel of polyurethaneurea fiber were evaluated as follows.

[25]

[26] Heat-set efficiency of polyurethaneurea yarns

[27] The produced yarns were stretched 100 % as exposed in the air, and were heated at 170 ℃ for 1 minute in an oven. After cooling to room temperature, the length of the yarns was measured and heat-set efficiency was calculated according to the following formula:

[28] Heat-set efficiency (%) = [(heat-set length - original length) / (stretched length - original length)] × 100

[29]

[30] NCO%

[31] NCO% = [100 × 2 × formula weight of NCO × (CR-1)] / [(molecular weight of di-isocyanate × CR) + molecular weight of polyol]

[32] Note) CR (capping ratio) = molar ratio of diisocyanate / molar ratio of polyol

[33]

[34] U%

[35] The produced yarns were mounted on a U% measurement apparatus (Keisokki Co.) and winded. After 20 seconds of unwinding, the thickness of yarns is measured with an evenness sensor and averaged. Average value is depicted as 0 % line in the chart. When the yarns are thicker than the average, points are marked over the 0 % line. And, when the yarns are thinner, they are marked below the 0 % line. U% is the deviation from the reference line as calculated from the area ratio. A smaller U% means superior yarn evenness.

[36]

[37] Workability

[38] Workability means the proportion of yarns with no defects of the total yarns produced a day. A higher workability means that good yarns with no defects such as cutting or twisting are produced.

[39]

[40] Selvage curling

[41] On circular knitted fabric made of nylon/polyurethaneurea elastic fiber, a regular triangle with one side being 5 cm is drawn. After scissoring two sides and spraying water, the fabric is dried. After drying the ratio of the curled area to the initial area is calculated.

[42] Selvage curling (%) = (area of curled triangle / area of original triangle) × 100

[43]

[44] Hand-feel of fabric

[45] Hand-feel of fabric is evaluated depending on sensual judgment. The inventors evaluated hardness, flexibility, elasticity, softness, drape, warmth or coolness, luster, etc. with eyes and hands in view that the articles are judged by experience.

[46]

[47] Example 1

[48] 32 g of 2,4'-diphenylmethanediisocyanate, 427 g of 4,4'-diphenylmethanediisocyanate and 2000 g of polytetramethylene ether glycol (molecular weight = 1800) were reacted with agitation at 90 ℃ for 180 minutes in nitrogen gas flow to produce a polyurethaneurea prepolymer having isocyanate groups on both ends thereof. The prepolymer was cooled to room temperature, and 3614 g of dimethylacetamide was added to produce a polyurethaneurea prepolymer solution.

Subsequently, 33.6 g (0.56 mol) of ethylenediamine, 10.4 g (0.14 mol) of 1,2-diaminopropane and 5.14 g of diethylamine were dissolved in 656 g of dimethylacetamide, and added to the prepolymer solution at 10 ℃ or below to produce a polyurethaneurea solution.

[49] Based on the solid content of the resultant polymer, 1.5 wt% of ethylenebis(oxyethylene)bis-(3-(5-*t*-butyl-4-hydroxy-*m*-toyl)-propionate), 0.5 wt% of 5,7-di-*t*-butyl-3-(3,4-dimethylphenyl)-3H-benzofuran-2-one, 1 wt% of 1,1,1,1-tetramethyl-4,4'-(methylene-di-*p*-phenylene)disemicarbazide, 1 wt% of poly(*N*, *N*-diethyl-2-aminoethyl methacrylate), and 0.1 wt% of titanium dioxide were added as a additive and mixed to produce a polyurethaneurea spinning solution.

[50] The spinning solution was then dry-spun (spinning temperature: 253 ℃) to produce 40 denier polyurethaneurea elastic fiber. Physical properties thereof were evaluated, and the results were shown in Table 1.

[51]

[52] Example 2

[53] 46 g of 2,4'-diphenylmethanediisocyanate, 413 g of 4,4'-diphenylmethanediisocyanate and 2000 g of polytetramethylene ether glycol (molecular weight = 1800) were reacted with agitation at 90 ℃ for 180 minutes in nitrogen gas flow to produce a polyurethaneurea prepolymer having isocyanate groups on both ends thereof. The prepolymer was cooled to room temperature, and 3614 g of dimethylacetamide was added to produce a polyurethaneurea prepolymer solution. Subsequently, 33.6 g (0.56 mol) of ethylenediamine, 10.4 g (0.14 mol) of 1,2-diaminopropane and 5.14 g of diethylamine were dissolved in 656 g of dimethylacetamide, and added to the prepolymer solution at 10 ℃ or below to produce a polyurethaneurea solution.

[54] Based on the solid content of the resultant polymer, 1.5 wt% of ethylenebis(oxyethylene)bis-(3-(5-*t*-butyl-4-hydroxy-*m*-toyl)-propionate), 0.5 wt% of 5,7-di-*t*-butyl-3-(3,4-dimethylphenyl)-3H-benzofuran-2-one, 1 wt% of 1,1,1,1-tetramethyl-4,4'-(methylene-di-*p*-phenylene)disemicarbazide, 1 wt% of poly(*N*, *N*-diethyl-2-aminoethyl methacrylate), and 0.1 wt% of titanium dioxide were added as a additive and mixed to produce a polyurethaneurea spinning solution.

[55] The spinning solution was then dry-spun (spinning temperature: 253 ℃) to produce 40 denier polyurethaneurea elastic fiber. Physical properties thereof were evaluated, and the results were shown in Table 1.

[56]

[57] Examples 3 and 4

[58] Polyurethaneurea elastic fiber was prepared in the same manner as in Example 1, except for changing the proportion of 2,4'-diphenylmethanediisocyanate to

4,4'-diphenylmethanediisocyanate. Physical properties thereof were evaluated in the same way, and the results were shown in Table 1.

[59]

[60] Example 5

[61] 80 g of 2,4'-diphenylmethanediisocyanate, 453 g of 4,4'-diphenylmethanediisocyanate and 2000 g of polytetramethylene ether glycol (molecular weight = 1800) were reacted with agitation at 90 ℃ for 180 minutes in nitrogen gas flow to produce a polyurethaneurea prepolymer having isocyanate groups on both ends thereof. The prepolymer was cooled to room temperature, and 3512 g of dimethylacetamide was added to produce a polyurethaneurea prepolymer solution. Subsequently, 46.6 g (0.78 mol) of ethylenediamine, 14.44 g (0.19 mol) of 1,2-diaminopropane and 7.5 g of diethylamine were dissolved in 909 g of dimethylacetamide, and added to the prepolymer solution at 10 ℃ or below to produce a polyurethaneurea solution. Addition of additives and spinning were performed in the same manner as in Example 1 to produce polyurethaneurea elastic fiber. Physical properties thereof were evaluated, and the results were shown in Table 1.

[62]

[63] Comparative Example 1

[64] 459 g of 4,4'-diphenylmethanediisocyanate and 2000 g of polytetramethylene ether glycol (molecular weight = 1800) were reacted with agitation at 90 ℃ for 180 minutes in nitrogen gas flow to produce a polyurethaneurea prepolymer having isocyanate groups on both ends thereof. The prepolymer was cooled to room temperature, and 3614 g of dimethylacetamide was added to produce a polyurethaneurea prepolymer solution. Subsequently, 33.6 g (0.56 mol) of ethylenediamine, 10.4 g (0.14 mol) of 1,2-diaminopropane and 5.14 g of diethylamine were dissolved in 656 g of dimethylacetamide, and added to the prepolymer solution at 10 ℃ or below to produce a polyurethaneurea solution. Addition of additives and spinning were performed in the same manner as in Example 1 to produce polyurethaneurea elastic fiber. Physical properties thereof were evaluated in the same way, and the results were shown in Table 1.

[65]

[66] Comparative Examples 2 and 3

[67] Polyurethaneurea elastic fiber was prepared in the same manner as in Example 1, except for changing the proportion of 2,4'-diphenylmethanediisocyanate to 4,4'-diphenylmethanediisocyanate. Physical properties thereof were evaluated in the same way, and the results were shown in Table 1.

[68]

[69] Table 1

[Table 1]

[Table]

	Mole % of 2,4'-MDI	NCO%	Heat-set efficiency	U% (yarn evenness)	Workability
Ex. 1	7	2.47	74	1.50	100 %
Ex. 2	10	2.47	80	1.76	100 %
Ex. 3	20	2.47	83	1.80	100 %
Ex. 4	25	2.47	87	1.85	98 %
Ex. 5	15	3.32	70	1.55	99 %
Comp. Ex. 1	0	2.47	52	2.0	100 %
Comp. Ex. 2	5	2.47	61	1.5	100 %
Comp. Ex. 3	30	3.32	87	3.10	86 %
*2,4'-MDI = 2,4'-diphenylmethanediisocyanate					

[70]

[71] As shown in Table 1, the polyurethaneurea elastic fiber comprising less than 7 mole % of 2,4'-diphenylmethanediisocyanate exhibited slightly lower heat-set efficiency. When the content of 2,4'-diphenylmethanediisocyanate was in excess of 25 mole %, heat-set efficiency was improved significantly, but yarn evenness reduced significantly and workability was poor.

[72]

[73] Examples 6 and 7

[74] Circular knitted fabrics were made from the elastic fiber prepared in Example 3 and nylon yarn, using a circular knitting machine (Mayer Co.) with 38 inches cylinder diameter, 28 gauge, 120 feeder. They were then treated under heat-setting conditions shown in Table 2. The selvage curling (%) and hand-feel of the resulting fabrics were evaluated, and the results were shown in Table 2. 70 denier nylon and 40 denier elastic fiber were used in preparing the circular knitted fabric. The content of the elastic fiber was 8 wt%, based on the total weight of the fabric.

[75]

[76] Comparative Examples 4 and 5

[77] Circular knitted fabrics were made in the same manner as in Example 6, except for using the elastic fiber prepared in Comparative Example 1 and changing heat-setting conditions as shown in Table 2. The selvage curling (%) and hand-feel of the resulting fabrics were evaluated in the same manner, and the results were shown in Table 2.

[78]

[79] Table 2

[Table 2]

[Table]

	Pre-setting temperature (℃)	Finish setting temperature (℃)	Selvage curling (%)	Hand-feel of fabric
Ex. 6	170	165	0	Superior
Ex. 7	175	160	0	Superior
Comp. Ex. 4	190	180	0	Poor
Comp. Ex. 5	180	170	100	Superior

[80]

[81] As shown in Table 2, in the process of preparing circular knitted nylon fabric, the fabric of Example 6 prepared with elastic fiber in Example 3 do not cause selvage curling even at about 20 ℃ lower heat-setting temperature, compared to the fabric in Comparative Example 4 prepared with elastic fiber in Comparative Example 1. Thus, a superior fabric with good hand-feel can be attained, without thermal degradation of nylon. Further, cost reduction can be attained by lowering the heat-setting temperature.

[82]

[83] The present invention has been described in detail with reference to preferred embodiments thereof. However, it will be appreciated by those skilled in the art that changes may be made in these embodiments without departing from the principles and spirit of the invention, the scope of which is defined in the appended claims and their equivalents.

Industrial Applicability

[84] The polyurethaneurea elastic fiber of the present invention has high heat-set efficiency at low temperature. Therefore, thermal degradation of the fiber that is weaved together with polyurethaneurea can be prevented with the heat-set process at low temperature, which resulted in superior hand-feel of the resulting fabric available in various areas.

Claims

[1] A method for preparing polyurethaneurea elastic fiber by polymerizing polyol with excessive amount of diisocyanate to produce a prepolymer (first polymerization), and dissolving the prepolymer in an organic solvent and then adding a chain extender and a chain terminator thereto (second polymerization) to produce polyurethaneurea elastic fiber, characterized in that the prepolymer is prepared by reacting a mixture of at least one diisocyanate comprising 4,4'-diphenylmethanediisocyanate and 7 to 25 mole % of 2,4'-diphenylmethanediisocyanate with polyol.

[2] The method according to claim 1, wherein the diisocyanate is at least one selected from the group consisting of 4,4'-diphenylmethanediisocyanate, 1,5'-naphthalenediisocyanate, 1,4'-phenylenediisocyanate, hexamethylenediisocyanate, 1,4'-cyclohexanediisocyanate, 4,4'-dicyclohexylmethanediisocyanate and isophoronediisocyanate.

[3] The method according to claim 1, wherein the polyol of the prepolymer is one selected from the group consisting of polytetramethylene ether glycol, polypropylene glycol, polycarbonate diol and a combination thereof.

[4] The method according to claim 1, wherein the chain extender is at least one selected from the group consisting of ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 2,3-diaminobutane, 1,5-diaminopentane, 10,6-hexamethylenediamine, 1,4-cyclohexanediamine and a combination thereof.

[5] The method according to claim 1, wherein weight proportion of isocyanate of the prepolymer is from 1.75 % to 4.13 %.

[6] Polyurethaneurea elastic fiber prepared by the method of claim 1, which has superior spinning workability, improved yarn evenness, and high heat-set efficiency at low temperature.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2007/006488

A. CLASSIFICATION OF SUBJECT MATTER

D01F 6/70(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)

IPC 8 D01F

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

Korean Utility models and applictions for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

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

eKIPASS(KIPO INTERNAL), Kyeword : "elastic, (yarn or fiber), diphenylmethane diisocyanate"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 07082608 A (Asahi Chem. Ind. Co. Ltd.) 28 March 1995 See the abstract and the claims	1-6
A	US 6472494 B2 (Nathan E. Houser et al.) 29 October 2002 See the abstract and the claims	1-6
A	US 5739252 A (Stephan Kirchmeyer et al.) 14 April 1998 See the abstract and the claims	1-6
A	KR 1020050050475 A (Tae Kwang Ind. Co. Ltd.) 31 May 2005 See the abstract and the claims	1-6

☐ 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
"E" earlier application or patent 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 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
25 JULY 2008 (25.07.2008)	**28 JULY 2008 (28.07.2008)**

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
CHOI Joong Hwan
Telephone No. 82-42-481-8408

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2007/006488

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 07082608 A	28-03-1995	None	
US 6472494 B2	29-10-2002	CN 1426431 A	25-06-2003
		DE 60112271 C0	01-09-2005
		EP 1276786 A2	22-01-2003
		HK 1056569 A1	08-04-2005
		KR 1020020095226 A	20-12-2002
		TW 589421 A	01-06-2004
		WO 200181443 A2	01-11-2001
US 5739252 A	14-04-1998	CA 2178055 A2	08-12-1996
		DE 19520731 A1	12-12-1996
		EP 747408 A1	11-12-1996
		ES 2139983 T3	16-02-2000
		JP 3887627 A	24-12-1996
KR 1020050050475 A	31-05-2005	CN 1621428 A	01-06-2005