

Description

Background of the Invention

1) Field of the Invention:

This invention relates to a plastic lens resin having a high refractive index (hereinafter may also be called «refractivity»), low dispersion, and either no or extremely little optical strain.

2) Description of the Prior Art:

Plastic lenses have been finding utility as eye lenses and camera lenses and in optical devices in recent years since they are lighter, less fragile and dyeable compared with inorganic lenses. As a resin employed widely for these applications these days, there is a resin obtained by subjecting diethylene glycol bisallylcarbonate (hereinafter called «CR-39») to radical polymerization. This resin has various merits such as excellent impact resistance, light weight, superb dyeability, and good machinability such as cutting, grinding and polishing machinability. Its refractive index is however small ($n_D = 1.50$) compared with inorganic lenses ($n_D = 1.52$). In order to achieve optical characteristics equivalent to glass lenses, it is essential to increase the central thickness, peripheral thickness and curvature of a lens, thereby unavoidably increasing the overall thickness of the lens. There is hence an outstanding demand for the development of a lens resin having a higher refractive index in order to overcome this inconvenience.

As lens resins which can purportedly materialize higher refractive indexes, there have been proposed urethane resins obtained respectively by a reaction between an isocyanate compound and a hydroxy compound such as diethylene glycol (Japanese Patent Laid-Open Nos. 136601/1982 and 136602/1982), a reaction between an isocyanate compound and a halogen-containing hydroxy compound such as tetrabromobisphenol A (Japanese Patent Laid-Open No. 164615/1983) and a reaction between an isocyanate compound and a sulfur-containing hydroxy compound (Japanese Patent Laid-Open Nos. 194401/1985 and 217229/1985); and S-alkyl thiocarbamate lens resins obtained individually by a reaction between an isocyanate compound and an aliphatic polythiol (Japanese Patent Laid-Open No. 199016/1985).

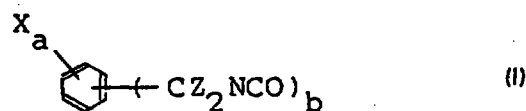
The S-alkyl thiocarbamate lens resins involve a few problems. They have large polymerization velocities even at relatively low temperatures and substantial difficulties are encountered in controlling the heat during their polymerization. Further, the resulting lenses have great optical strain. It is hence difficult to provide useful lenses.

Summary of the Invention

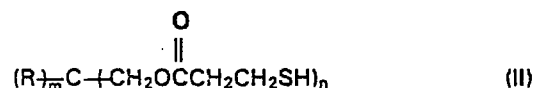
With the foregoing in view, the present inventors have conducted an investigation with respect to a variety of polythiols. As a result, it has been found that a resin, which is obtained by reacting at least one polyisocyanate represented by the below-described general formula (I) with at least one polythiol represented by the below-described general for-

mula (II) and/or at least one polythiol represented by the below-described general formula (III), features milder progress of its polymerization reaction and hence easier polymerization and moreover develops either no or extremely little optical strain subsequent to its polymerization compared with the S-alkyl thiocarbamate lens resins while retaining comparable light weight property, high refractive index, low dispersion, excellent transparency, impact resistance, weather-ability and machinability, leading to completion of this invention.

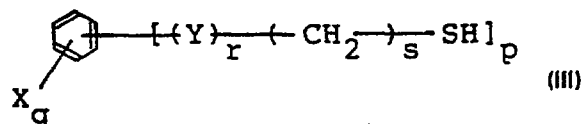
In one aspect of this invention, there is thus provided a high-refractivity plastic lens resin obtained by polymerizing under heat at least one polyisocyanate represented by the following general formula (I):



wherein X means a hydrogen, chlorine or bromine atom or a methyl or ethyl group, Z is a hydrogen atom or a methyl group, a stands for an integer of 1-4, b is an integer of 2-4, and a + b is not greater than 6 (a + b ≤ 6), with at least one polythiol represented by the following general formula (II):



wherein R means a methyl, ethyl, chloromethyl or bromomethyl group, m stands for an integer of 0-2, n is 4 - m and/or at least one polythiol represented by the following general formula (III):



wherein X means a hydrogen, chlorine or bromine atom or a methyl or ethyl group, Y denotes an oxygen or sulfur atom, r stands for 0 or 1, s is an integer of 0-2, p is an integer of 2-4, q is an integer of 1-4 and p + q is not greater than 6 (p + q ≤ 6), in such amounts that the -NCO/-SH molar ratio falls within 0.5-3.0.

Detailed Description of the Invention and Preferred Embodiments

Illustrative specific examples of the compound which is represented by the general formula (I) and is useful in the practice of this invention may include compound such as o-xylylene diisocyanate, m-xylylene diisocyanate, p-xylylene diisocyanate, 1,3-bis(α,α-dimethylisocyanatemethyl)benzene, 1,4-bis(α,α-dimethylisocyanatemethyl)benzene and mesitylene triisocyanate as well as their nucleus-chlorinated, brominated, methylated and ethylated derivatives. The derivatives may specifically include 4-chloro-m-xylylene diisocyanate, 4,5-dichloro-m-xylylene diisocyanate, 2,3,5,6-tetrabromo-p-xylylene diisocyanate, 4-methyl-m-xylylene di-

isocyanate, 4-ethyl-m-xylylene diisocyanate, etc. As illustrative specific examples of the compound represented by the general formula (II), may be mentioned pentaerythritol tetrakis(mercaptopropionate), trimethylolpropane tris(mercaptopropionate), trimethyloethane tris(mercaptopropionate), dichloroneopentylglycol bis(mercaptopropionate) and dibromoneopentylglycol bis(mercaptopropionate).

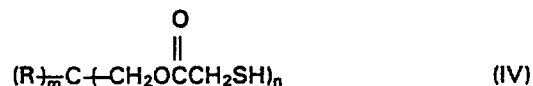
On the other hand, illustrative specific examples of the compound represented by the general formula (III) may include:

1,2-dimercaptobenzene;
 1,3-dimercaptobenzene;
 1,4-dimercaptobenzene;
 1,2-bis(mercaptomethylene)benzene;
 1,3-bis(mercaptomethylene)benzene;
 1,4-bis(mercaptomethylene)benzene;
 1,2-bis(mercaptoethylene)benzene;
 1,3-bis(mercaptoethylene)benzene;
 1,4-bis(mercaptoethylene)benzene;
 1,2-bis(mercaptomethylenoxy)benzene;
 1,3-bis(mercaptomethylenoxy)benzene;
 1,4-bis(mercaptomethylenoxy)benzene;
 1,2-bis(mercaptoethylenoxy)benzene;
 1,3-bis(mercaptoethylenoxy)benzene;
 1,4-bis(mercaptoethylenoxy)benzene;
 1,2-bis(mercaptomethylenethio)benzene;
 1,3-bis(mercaptomethylenethio)benzene;
 1,4-bis(mercaptomethylenethio)benzene;
 1,2-bis(mercaptoethylenethio)benzene;
 1,3-bis(mercaptoethylenethio)benzene;
 1,4-bis(mercaptoethylenethio)benzene;
 1,2,3-trimercaptobenzene;
 1,2,4-trimercaptobenzene;
 1,3,5-trimercaptobenzene;
 1,2,3-tris(mercaptomethylene)benzene;
 1,2,4-tris(mercaptomethylene)benzene;
 1,3,5-tris(mercaptomethylene)benzene;
 1,2,3-tris(mercaptoethylene)benzene;
 1,2,4-tris(mercaptoethylene)benzene;
 1,3,5-tris(mercaptoethylene)benzene;
 1,2,3-tris(mercaptomethylenoxy)benzene;
 1,2,4-tris(mercaptomethylenoxy)benzene;
 1,3,5-tris(mercaptomethylenoxy)benzene;
 1,2,3-tris(mercaptoethylenoxy)benzene;
 1,2,4-tris(mercaptoethylenoxy)benzene;
 1,3,5-tris(mercaptoethylenoxy)benzene;
 1,2,3-tris(mercaptomethylenethio)benzene;
 1,2,4-tris(mercaptomethylenethio)benzene;
 1,3,5-tris(mercaptomethylenethio)benzene;
 1,2,3-tris(mercaptoethylenethio)benzene;
 1,2,4-tris(mercaptoethylenethio)benzene;
 1,3,5-tris(mercaptoethylenethio)benzene;
 1,2,3,4-tetramercaptobenzene;
 1,2,3,5-tetramercaptobenzene;
 1,2,4,5-tetramercaptobenzene;
 1,2,3,4-tetrakis(mercaptomethylene)benzene;
 1,2,3,5-tetrakis(mercaptomethylene)benzene;
 1,2,4,5-tetrakis(mercaptomethylene)benzene;
 1,2,3,4-tetrakis(mercaptoethylene)benzene;
 1,2,3,5-tetrakis(mercaptoethylene)benzene;
 1,2,4,5-tetrakis(mercaptoethylene)benzene;
 1,2,3,4-tetrakis(mercaptomethylenoxy)benzene;
 1,2,3,5-tetrakis(mercaptomethylenoxy)benzene;

1,2,4,5-tetrakis(mercaptomethylenoxy)benzene;
 1,2,3,4-tetrakis(mercaptoethylenoxy)benzene;
 1,2,3,5-tetrakis(mercaptoethylenoxy)benzene;
 1,2,4,5-tetrakis(mercaptoethylenoxy)benzene;
 1,2,3,4-tetrakis(mercaptomethylenethio)benzene;
 1,2,3,5-tetrakis(mercaptomethylenethio)benzene;
 1,2,4,5-tetrakis(mercaptomethylenethio)benzene;
 1,2,3,4-tetrakis(mercaptoethylenethio)benzene;
 1,2,3,5-tetrakis(mercaptoethylenethio)benzene;
 1,2,4,5-tetrakis(mercaptoethylenethio)benzene.

The nucleus-chlorinated, brominated, methylated and ethylated derivatives of the above exemplified specific compounds may also be mentioned as exemplary compound (III). As specific examples of such derivatives, may be mentioned 3-chloro-1,2-dimercaptobenzene, 4-chloro-1,2-dimercaptobenzene, 3,5-dichloro-1,2-dimercaptobenzene, 3,4,5-tribromo-1,2-dimercaptobenzene, 5-methyl-1,3-dimercaptobenzene, 5-ethyl-1,3-dimercaptobenzene, 2,3,4,6-tetrachloro-1,5-bis-(mercaptomethylene)benzene, etc.

At least one polyisocyanate represented by the general formula (I) is reacted with at least one polythiol represented by the general formula (II) and/or at least one polythiol represented by the general formula (III) in such amount that the -NCO/-SH ratio falls within a range of 0.5-3.0, preferably, within a range of 0.5-1.5. In order to improve various properties, especially, the heat resistance, less than 20 mole % of the polyisocyanate represented by the general formula (I) may be replaced by an aromatic isocyanate such as a tolyene diisocyanate or diphenylmethane diisocyanate in the present invention. Furthermore, less than 20 mole % of the polythiol represented by the general formula (II) may also be replaced by another thiol represented by the following general formula (IV):



wherein R, m and n have the same meaning as defined above, or a polyol such as trimethylol propane or trimethylol ethane. If the proportion of the replacement compound, namely, the aromatic isocyanate, the polythiol represented by the general formula (IV) or the polyol such as trimethylol propane exceeds 20 mole %, the optical strain is increased and the control of the heat during the polymerization is rendered more complex. It is hence not preferable to use the replacement compound in such an excess proportion.

In the present invention, it is also possible to incorporate, for improved weatherability, additives such as ultraviolet ray absorbent, oxidation inhibitor, coloring inhibitor and fluorescent dye as needed. The resin of this invention can be dyed readily with an ordinary dispersible dye in water or a solvent. In order to facilitate its dyeing, it is also feasible to add a carrier or to heat the water or solvent.

For the production of the lens resin of this invention, at least one polyisocyanate represented by the general formula (I) is added with at least one poly-

thiol represented by the general formula (II) and/or at least one polythiol represented by the general formula (III). The above-mentioned aromatic polyisocyanate, polyol or polythiol and additives may also be added in accordance with physical properties required. The resultant mixture is then processed by a known cast-molding technique, namely, is poured in a mold formed in combination of a metal mold and a resin gasket, followed by its heating and curing. Here, a mold release agent may be applied to the mold or may be incorporated in the mixture so as to facilitate the release of the resulting resin after the molding. The reaction time and temperature vary depending on the types of monomers to be used. However, they are generally $-20 - 150^{\circ}$ and 0.5 hr. - 72 hrs. respectively.

The thus-obtained lens resin of this invention is colorless and transparent and has a high refractive index, low dispersion and low specific gravity. It is excellent in impact resistance and weatherability. Moreover, its polymerization is easy. It is free of optical strain, and is excellent in machinability such as polishing machinability and also in dyeability. It is hence suitable for use as eyeglass lenses and camera lenses and in other optical devices.

The present invention will be described in more detail by the following Examples. The refractive index, Abbe number, lens polishing machinability, impact resistance and yellowing resistance upon exposure to ultra violet rays of a lens resin obtained in each of the following Examples were measured or determined respectively in accordance with the following testing methods.

Refractive index and Abbe number:

Measured at 20°C by means of a Pulfrich refractometer.

Machinability:

The resin was ground and polished by a lens polisher for eyeglass lenses. The machinability is rated good (O) where the thus-polished surface was good, whereas the machinability is rated fair (Δ) where the thus-polished surface was fair.

Impact resistance:

Using a flat plate having a central thickness of 2 mm, a falling ball impact test was conducted in accordance with the FDA standards. The impact resistance is rated good (O) where the flat plate did not shatter.

Ultraviolet light resistance:

A lens was mounted on weather-o-meter equipped with sunshine carbon arc lamps. Upon an elapsed

time of 200 hours, the lens was removed from the weather-o-meter and its hue was compared with the hue of a lens before the test on the weather-o-meter. The following ranking standard was followed.

5	No change	O
	Slight yellowing	Δ
	Substantial yellowing	X

10 Optical strain:

Determined visually by means of an optical strain meter. The following ranking standard was followed.

15	No optical strain	O
	Noticeable optical strain	X

Example 1

20 Uniformly mixed at room temperature were 9.4 g (0.050 mole) of m-xylylene diisocyanate and 7.1 g (0.050 mole) of 1,2-dimercaptobenzene. The resultant mixture was poured into a mold, which was formed of a glass mold treated with a mold release agent of the baking silicone type and a TEFLON (trade mark) gasket.

25 The mixture was heated at 45°C for 3 hours, at 60°C for 2 hours and then at 80°C for 2 hours. The thus-obtained lens had a refractive index of 1.66, an Abbe number of 28 and a specific gravity of 1.32. It was colorless and transparent, excellent in machinability, impact resistance and ultraviolet light resistance, and free of optical strain.

Example 2-23

35 Following the procedure of Example 1, lenses were produced separately from the compositions given in Tables 1 and 2. Test results are also shown in the same tables.

40 Comparative Example 1

45 An attempt was made to mix 9.4 (0.050 mole) of m-xylylene diisocyanate with 10.8 g (0.025 mole) of pentaerythritol tetrakis(thioglycolate) while cooling them at -10°C . It was however unable to mix them due to unduly high viscosity. When the temperature was hence raised approximately to room temperature, they underwent polymerization with violent generation of heat. The refractive index and Abbe number of the resultant lens were 1.60 and 34 respectively but substantial optical strain was contained.

Comparative Examples 2-4:

55 Following the procedure of Comparative Example 1, lenses were produced separately from the compositions given in Tables 1 and 2. Test results are also shown in the same tables.

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65

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TABLE 1

Ex.	Polyisocyanate (mole)		Polythiol (mole)	Additive (mole)	Refractive index, n_D^{20}	Abbe number	Specific gravity	Machin- ability
2	m-XDI ¹⁾	(0.050)	1,2,3-trimercapto- benzene (0.033)	—	1.67	28	1.31	0
3	m-XDI p-XDI ²⁾	(0.035) (0.015)	4-methyl-1,2-dimer- captobenzene (0.050)	—	1.65	30	1.32	0
4	m-XDI	(0.050)	3,6-dichloro-1,2-di- mercapto- benzene (0.040)	—	1.66	29	1.34	0
5	m-XDI	(0.050)	3,4,6-trichloro-1,2-di- mercaptobenzene (0.040)	TMP ³⁾ (0.007)	1.65	29	1.36	0
6	m-XDI	(0.050)	1,4-bis(mercapto- methylene)-benzene (0.030, PEMP ⁴⁾ (0.010)	—	1.63	31	1.31	0
7	m-XDI	(0.050)	1,3-bis(mercapto- methylene)-benzene (0.040)	PETG ⁵⁾ (0.005) UV absorbent [1]*	1.65	30	1.31	0
8	m-XDI	(0.050)	2,4,5,6-tetrachloro- -1,3-bis(mercapto- methylene)-benzene (0.050)	—	1.67	29	1.38	0
9	m-XDI	(0.050)	1,2-bis(mercapto- ethylene)benzene (0.040) PEMP (0.01)	—	1.62	34	1.31	0
10	m-XDI	(0.050)	1,3-bis(mercapto- methylenoxy)benzene (0.030)	TMP (0.013)	1.64	32	1.30	0
11	m-XDI	(0.050)	1,3-bis(mercapto- methylenethio)- benzene (0.050)	—	1.66	30	1.32	0
12	TC-m-XDI ⁶⁾	(0.050)	1,2-dimercapto- benzene (0.040)	PETG (0.01)	1.66	31	1.39	0
13	4-methyl-m-XDI ⁷⁾	(0.050)	1,2-dimercapto- benzene (0.040)	PETG (0.01)	1.63	33	1.32	0
14	m-XDI	(0.050)	PEMP (0.025)	—	1.59	36	1.31	0
15	m-XDI (0.045, tolylene diisocyanate (0.005)		PEMP (0.025)	—	1.60	35	1.31	0
16	TC-m-XDI	(0.050)	PEMP (0.030)	—	1.61	34	1.34	0
17	m-XDI	(0.050)	TMPMP ⁸⁾ (0.033)	—	1.59	35	1.30	0
18	m-XDI	(0.050)	TMEMP ⁹⁾ (0.033)	—	1.59	35	1.29	0
19	4-methyl-m-XDI (0.050)		PEMP (0.025)	—	1.59	36	1.32	0
20	m-XDI	(0.050)	DCNPMP ¹⁰⁾ (0.050)	—	1.60	39	1.37	0
21	m-XDI	(0.050)	BCNPMP ¹¹⁾ (0.050)	—	1.61	40	1.41	0

* wt. % based on the sum of the weights of the polyisocyanate and polythiol used.

TABLE 1 (continued)

Ex.	Polyisocyanate (mole)	Polythiol (mole)	Additive (mole)	Refractive index, n_D^{20}	Abbe number	Specific gravity	Machinability
22	1,3-bis(α,α -dimethylisocyanatemethyl)-benzene (0.050)	PEMP (0.025)	—	1.57	39	1.32	O
23	1,3-bis(α,α -dimethylisocyanatemethyl)-benzene (0.050)	1,3-bis(mercaptomethylene)benzene (0.035), PEMP (0.008)	—	1.60	36	1.32	O

Comp. Ex.	Polyisocyanate (mole)	Polythiol (mole)	Additive (mole)	Refractive index, n_D^{20}	Abbe number	Specific gravity	Machinability
1	m-XDI (0.050)	PETG (0.025)	—	1.60	34	1.44	O
2	m-XDI (0.025), tolylene diisocyanate (0.025)	PETG (0.025)	—	1.61	29	1.43	O
3	m-XDI (0.050)	TMTG ¹²⁾ (0.033)	—	1.60	34	1.33	O
4	m-XDI (0.050)	di(2-mercaptoethyl)-ether (0.050)	—	1.62	33	1.34	O

TABLE 2

Ex.	Polyisocyanate (mole)	Polythiol (mole)	Additive (mole)	Impact-resistance	UV light resistance	Appearance	Optical strain
2	m-XDI ¹⁾ (0.050)	1,2,3-trimercaptobenzene (0.033)	—	O	O	colorless transparent	O
3	m-XDI (0.035) p-XDI ²⁾ (0.015)	4-methyl-1,2-dimercaptobenzene (0.050)	—	O	O	ditto	O
4	m-XDI (0.050)	3,6-dichloro-1,2-dimercaptobenzene (0.040)	—	O	O	ditto	O
5	m-XDI (0.050)	3,4,6-trichloro-1,2-dimercaptobenzene (0.040)	TMP ³⁾ (0.007)	O	O	ditto	O
6	m-XDI (0.050)	1,4-bis(mercaptomethylene)-benzene (0.030), PEMP ⁴⁾ (0.010)	—	O	O	ditto	O
7	m-XDI (0.050)	1,3-bis(mercaptomethylene)-benzene (0.040)	PETG ⁵⁾ (0.005) UV absorbent [1]*	O	O	ditto	O
8	m-XDI (0.050)	2,4,5,6-tetrachloro-1,3-bis(mercaptomethylene)-benzene (0.050)	—	O	O	colorless transparent	O

* wt. % based on the sum of the weights of the polyisocyanate and polythiol used.

TABLE 2 (continued)

Ex.	Polyisocyanate (mole)	Polythiol (mole)	Additive (mole)	Impact- resis- tance	UV light resis- tance	Appearance	Optical strain
9	m-XDI (0.050)	1,2-bis(mercaptoethyl- ene)-benzene (0.040), PEMP (0.01)	—	O	O	ditto	O
10	m-XDI (0.050)	1,3-bis(mercaptomethyl- enoxy)benzene (0.030)	TMP (0.013)	O	O	ditto	O
11	m-XDI (0.050)	1,3-bis(mercaptomethyl- enethio)benzene (0.050)	—	O	O	ditto	O
12	TC-m-XDI ⁶⁾ (0.050)	1,2-dimercaptobenzene (0.040)	PETG (0.01)	O	O	ditto	O
13	4-methyl-m-XDI ⁷⁾ (0.050)	1,2-dimercaptobenzene (0.040)	PETG (0.01)	O	O	ditto	O
14	m-XDI (0.050)	PEMP (0.025)	—	O	O	colorless transparent	O
15	m-XDI (0.045) tolylene diisocyanate (0.005)	PEMP (0.025)	—	O	O	ditto	O
16	TC-m-XDI (0.050)	PEMP (0.030)	—	O	O	ditto	O
17	m-XDI (0.050)	TMPMP ⁸⁾ (0.033)	—	O	O	ditto	O
18	m-XDI (0.050)	TMEMP ⁹⁾ (0.033)	—	O	O	ditto	O
19	4-methyl-m-XDI (0.050)	PEMP (0.025)	—	O	O	ditto	O
20	m-XDI (0.050)	DCNMPMP ¹⁰⁾ (0.050)	—	O	O	ditto	O
21	m-XDI (0.050)	BCNMPMP ¹¹⁾ (0.050)	—	O	O	ditto	O
22	1,3-bis-(α,α -dimethyl- isocyanatemethyl)- benzene (0.050)	PEMP (0.025)	—	O	O	ditto	O
23	1,3-bis-(α,α -dimethyl- isocyanatemethyl)- benzene (0.050)	1,3-bis(mercaptomethyl- ene)benzene (0.035), PEMP (0.008)	—	O	O	ditto	O

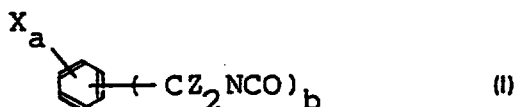
Comp. Ex.	Polyisocyanate (mole)	Polythiol (mole)	Additive (mole)	Impact- resis- tance	UV light resis- tance	Appearance	Optical strain
1	m-XDI (0.050)	PETG (0.025)	—	O	O	colorless transparent	X
2	m-XDI (0.025), tolylene diisocyanate (0.025)	PETG (0.025)	—	O	X	ditto	X
3	m-XDI (0.050)	TMTG ¹²⁾ (0.033)	—	O	O	ditto	X
4	m-XDI (0.050)	di(2-mercaptoethyl ether (0.050)	—	O	O	ditto	X

Note:

¹⁾ m-Xylylene diisocyanate.²⁾ p-Xylylene diisocyanate.³⁾ Trimethylol propane.⁴⁾ Pentaerythritol tetrakis(mercaptopropionate).⁵⁾ Pentaerythritol tetrakis(thioglycolate).⁶⁾ Tetrachloro-m-xylylene diisocyanate.⁷⁾ 4-methyl-m-xylylene diisocyanate.⁸⁾ Trimethylolpropane tris(mercaptopropionate).⁹⁾ Trimethylolethane tris(mercaptopropionate).¹⁰⁾ Dichloroneopentylglycol bis(mercaptopropionate).¹¹⁾ Dibromoneopentylglycol bis(mercaptopropionate).¹²⁾ Trimethylolpropane tris(thioglycolate).

Claims

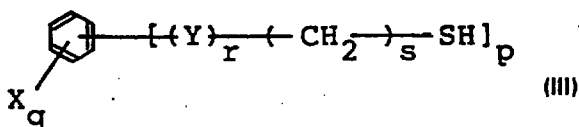
1. A high-refractivity plastic lens resin obtained by polymerizing under heat at least one polyisocyanate represented by the following general formula (I):



wherein X means a hydrogen, chlorine or bromine atom or a methyl or ethyl group, Z is a hydrogen atom or a methyl group, a stands for an integer of 1-4, b is an integer of 2-4, and $a + b$ is not greater than 6 ($a + b \leq 6$), with at least one polythiol represented by the following general formula (II):



wherein R means a methyl, ethyl, chloromethyl or bromomethyl group, m stands for an integer of 0-2, n is 4 - m and/or at least one polythiol represented by the following general formula (III):



wherein X means a hydrogen, chlorine or bromine atom or a methyl or ethyl group, Y denotes an oxygen or sulfur atom, r stand for 0 or 1, s is an integer of 0-2, p is an integer of 2-4, q is an integer of 1-4 and $p + q$ is not greater than 6 ($p + q \leq 6$), in such amounts that the -NCO/-SH molar ratio falls within 0.5-3.0.

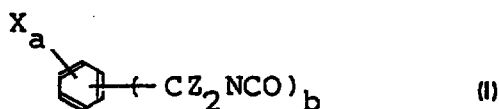
2. The high-refractivity plastic lens resin as claimed in Claim 1, wherein less than 20 mole % of the polyisocyanate represented by the general formula (I) is replaced by a tolylene diisocyanate.

3. The high-refractivity plastic lens resin as claimed in Claim 1, wherein less than 20 mole % of the polythiol represented by the general formula (II) is replaced by a polythiol represented by the following general formula (IV):



wherein R, m and n have the same meaning as defined in Claim 1.

4. A lens comprising a copolymer obtained by polymerizing under heat at least one polyisocyanate represented by the following general formula (I):

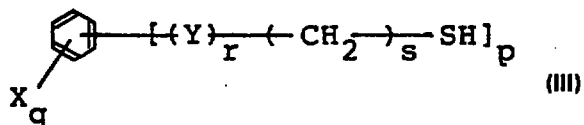


wherein X means a hydrogen, chlorine or bromine atom or a methyl or ethyl group, Z is a hydrogen atom

or a methyl group, a stands for an integer of 1-4, b is an integer of 2-4, and $a + b$ is not greater than 6 ($a + b \leq 6$), with at least one polythiol represented by the following general formula (II):



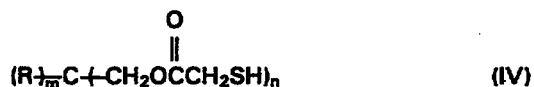
wherein R means a methyl, ethyl, chloromethyl or bromomethyl group, m stands for an integer of 0-2 and n is 4 - m and/or at least one polythiol represented by the following general formula (III):



wherein X means a hydrogen, chlorine or bromine atom or a methyl or ethyl group, Y denotes an oxygen or sulfur atom, r stands for 0 or 1, s is an integer of 0-2, p is an integer of 2-4, q is an integer of 1-4 and $p + q$ is not greater than 6 ($p + q \leq 6$), in such amounts that the -NCO/-SH molar ratio falls within 0.5-3.0.

5. The lens as claimed in Claim 4, wherein less than 20 mole % of the polyisocyanate represented by the general formula (I) is replaced by a tolylene diisocyanate.

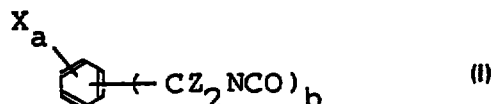
6. The lens as claimed in Claim 4, wherein less than 20 mole % of the polythiol represented by the general formula (II) is replaced by a polythiol represented by the following general formula (IV):



wherein R, m and n have the same meaning as defined in Claim 4.

Patentansprüche

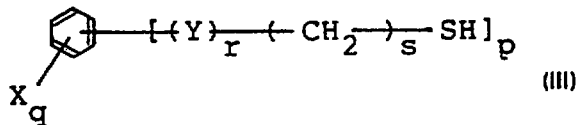
1. Harz mit einem hohen Brechungsindex für Linsen aus Kunststoff, das durch Polymerisieren unter Anwendung von Wärme wenigstens eines Polyisocyanats, das durch die folgende allgemeine Formel (I) dargestellt wird:



wobei X ein Wasserstoff-, Chlor- oder Bromatom oder eine Methyl- oder Ethylgruppe bezeichnet, Z ein Wasserstoffatom oder eine Methylgruppe ist, a für eine ganze Zahl von 1-4 steht, b eine ganze Zahl von 2-4 ist und $a + b$ nicht größer als 6 ist ($a + b \leq 6$), mit wenigstens einem Polythiol, das durch die folgende allgemeine Formel (II) dargestellt wird:



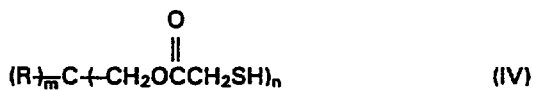
worin R eine Methyl-, Ethyl-, Chlormethyl- oder Brommethylgruppe bezeichnet, m für eine ganze Zahl von 0-2 steht, n 4 - m ist, und/oder wenigstens einem Polythiol, das durch die folgende allgemeine Formel (III) dargestellt wird:



worin X ein Wasserstoff-, Chlor- oder Bromatom oder eine Methyl- oder Ethylgruppe bezeichnet, Y ein Sauerstoff- oder Schwefelatom bezeichnet, r für 0 oder 1 steht, s eine ganze Zahl von 0-2 ist, p eine ganze Zahl von 2-4 ist, q eine ganze Zahl von 1-4 ist und p + q nicht größer als 6 ist (p + q ≤ 6), in solchen Mengen, daß das molare Verhältnis -NCO/-SH in den Bereich von 0,5-3,0 fällt, erhalten wird.

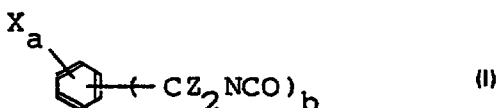
2. Harz mit einem hohen Brechungsindex für Linsen aus Kunststoff nach Anspruch 1, bei dem weniger als 20 Mol.-% des Polyisocyanats, das durch die allgemeine Formel (I) dargestellt wird, durch ein Tolyldiisocyanat ersetzt ist.

3. Harz mit einem hohen Brechungsindex für Linsen aus Kunststoff nach Anspruch 1, bei dem weniger als 20 Mol.-% des Polythiols, das durch die allgemeine Formel (II) dargestellt wird, durch ein Polythiol, das durch die folgende allgemeine Formel (IV) dargestellt wird:



worin R, m und n die gleichen Bedeutungen besitzen, wie sie in Anspruch 1 definiert sind, ersetzt worden ist.

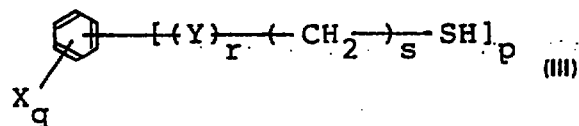
4. Eine Linse, die ein Copolymer umfaßt, das durch Polymerisieren unter Anwendung von Wärme wenigstens eines Polyisocyanats, das durch die folgende allgemeine Formel (I) dargestellt wird:



worin X ein Wasserstoff-, Chlor- oder Bromatom oder eine Methyl- oder Ethylgruppe bezeichnet, Z ein Wasserstoffatom oder eine Methylgruppe ist, a für eine ganze Zahl von 1-4 steht, b eine ganze Zahl von 2-4 ist und a + b nicht größer als 6 ist (a + b ≤ 6), mit wenigstens einem Polythiol, das durch die folgende allgemeine Formel (II) dargestellt wird:



worin R eine Methyl-, Ethyl-, Chlormethyl- oder Brommethylgruppe bezeichnet, m für eine ganze Zahl von 0-2 steht und n 4 - m ist, und/oder wenigstens einem Polythiol, das durch die folgende allgemeine Formel (III) dargestellt wird:



worin X ein Wasserstoff-, Chlor- oder Bromatom oder eine Methyl- oder Ethylgruppe bezeichnet, Y ein Sauerstoff- oder Schwefelatom bezeichnet, r für 0 oder 1 steht, s eine ganze Zahl von 0-2 ist, p eine ganze Zahl von 2-4 ist, q eine ganze Zahl von 1-4 ist und p + q nicht größer als 6 ist (p + q ≤ 6), in solchen Mengen, daß das molare Verhältnis -NCO/-SH in den Bereich von 0,5-3,0 fällt, erhalten worden ist.

5. Linse nach Anspruch 4, bei der weniger als 20 Mol.-% des Polyisocyanats, das durch die allgemeine Formel (I) dargestellt wird, durch ein Tolyldiisocyanat ersetzt ist.

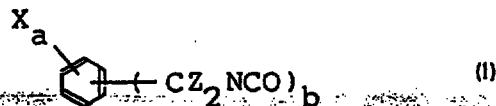
6. Linse nach Anspruch 4, bei der weniger als 20 Mol.-% des Polythiols, das durch die allgemeine Formel (II) dargestellt wird, durch ein Polythiol, das durch die folgende allgemeine Formel (IV) dargestellt wird:



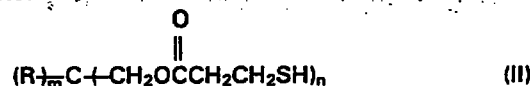
worin R, m und n die gleichen Bedeutungen besitzen, wie sie in Anspruch 4 definiert sind, ersetzt worden ist.

Revendications

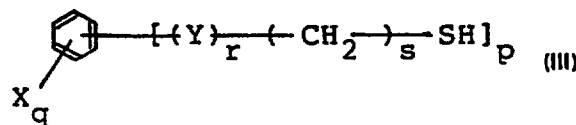
1. Une résine pour lentilles en matière plastique à haute réfringence obtenue par polymérisation à chaud d'au moins un polyisocyanate représenté par la formule générale (I) suivante:



dans laquelle X représente un atome d'hydrogène, de chlore ou de brome ou un groupe méthyle ou éthyle, Z est un atome d'hydrogène ou un groupe méthyle, a est un entier de 1 à 4, b est un entier de 2 à 4 et a + b ne dépasse pas 6 (a + b ≤ 6), avec au moins un polythiol représenté par la formule générale (II) suivante:



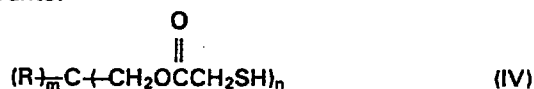
dans laquelle R représente un groupe méthyle, éthyle, chlorométhyle ou bromométhyle, m représente un entier de 0 à 2 et n est 4 - m, et/ou au moins un polythiol représenté par la formule générale (III) suivante:



dans laquelle X représente un atome d'hydrogène, de chlore ou de brome ou un groupe méthyle ou éthyle, Y représente un atome d'oxygène ou de soufre, r représente 0 ou 1, s est un entier de 0 à 2, p est un entier de 2 à 4, q est un entier de 1 à 4 et p + q ne dépasse pas 6 ($p + q \leq 6$), en des quantités telles que le rapport molaire -NCO/-SH soit compris entre 0,5 et 3,0.

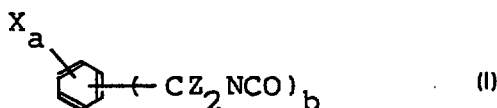
2. La résine pour lentilles en matière plastique à haute réfringence selon la revendication 1, dans laquelle moins de 20% molaires du polyisocyanate, représenté par la formule générale (I), sont remplacés par un tolylène diisocyanate.

3. La résine pour lentilles en matière plastique à haute réfringence selon la revendication 1, dans laquelle moins de 20% molaires du polythiol, représenté par la formule générale (II), sont remplacés par un polythiol représenté par la formule générale (IV) suivante:



dans laquelle R, m et n ont les mêmes significations que celles définies dans la revendication 1.

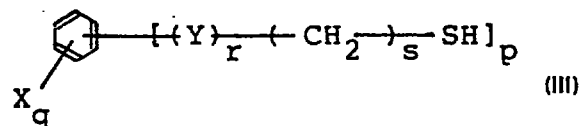
4. Une lentille comprenant un copolymère obtenu par polymérisation à chaud d'au moins un polyisocyanate représenté par la formule générale (I):



dans laquelle X représente un atome d'hydrogène, de chlore ou de brome ou un groupe méthyle ou éthyle, Z est un atome d'hydrogène ou un groupe méthyle, a est un entier de 1 à 4, b est un entier de 2 à 4 et a + b ne dépasse pas 6 ($a + b \leq 6$), avec au moins un polythiol représenté par la formule générale (II) suivante:



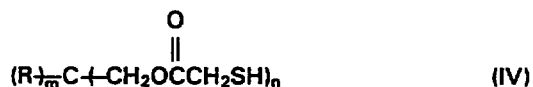
dans laquelle R représente un groupe méthyle, éthyle, chlorométhyle ou bromométhyle, m représente un entier de 0 à 2 et n est 4 - m, et/ou au moins un polythiol représenté par la formule générale (III) suivante:



dans laquelle X représente un atome d'hydrogène, de chlore ou de brome ou un groupe méthyle ou éthyle, Y représente un atome d'oxygène ou de soufre, r représente 0 ou 1, s est un entier de 0 à 2, p est un entier de 2 à 4, q est un entier de 1 à 4 et p + q ne dépasse pas 6 ($p + q \leq 6$), en des quantités telles que le rapport molaire -NCO/-SH soit compris entre 0,5 et 3,0.

5. La lentille selon la revendication 4, dans laquelle moins de 20% molaires du polyisocyanate représenté par la formule générale (I) sont remplacés par un tolylène diisocyanate.

6. La lentille selon la revendication 4, dans laquelle moins de 20% molaires du polythiol représenté par la formule générale (II) sont remplacés par un polythiol représenté par la formule générale (IV) suivante:



dans laquelle R, m et n ont les mêmes significations que celles définies dans la revendication 4.

