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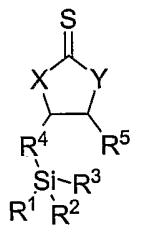
(54) Title: SILOXANE DERIVATIVES OF 1,3-OXATHIOLANE-2-THIONES, THEIR PREPARATION AND USE THEREOF



(I)

(57) Abstract: The present invention relates to 1,3-oxathiolane-2-thione compounds of the general formula (I): wherein R^1 and R^2 are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue, R^3 is different or the same as R^1 or R^2 or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, or an araliphatic or heteroaraliphatic residue, R^4 is a bridging group selected from the groups consisting of aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic and heteroaromatic groups and R^5 is hydrogen, an aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic, heteroaromatic, cycloaliphatic or heterocycloaliphatic group or R^4 and R^5 form a cycloaliphatic, cycloheteroaliphatic, aromatic or heteroaromatic residue, which is optionally substituted with an aliphatic, heteroaliphatic residue serving as a bridging group to the silicone atom and X and Y are different and selected from oxygen and sulfur and mixtures of such compounds. A further objective is to provide a method of production of such compounds, compounds synthesized from the 1,3-oxathiolane2-thiones and their use in a variety of coating and bonding applications.

SILOXANE DERIVATIVES OF 1,3-OXATHIOLANE-2-THIONES, THEIR PREPARATION AND USE THEREOF

The present invention relates to a novel class of 1,3-oxathiolane-2-thione key intermediate compounds and compounds produced thereof, a method of the manufacture of the novel 1,3-oxathiolane-2-thiones and their use as and in coatings, sealants, primers and adhesion promoters for coating and bonding of various metallic and non-metallic materials.

There is a big need to provide surfaces with primers and other coatings to equip the substrate with anti-corrosive and moisture insensitive characteristics as well as enhanced adhesion properties. Moreover compounds are needed to act as adhesion promoters and adhesive agents showing an excellent curability combined with a multitude of modification possibilities to ensure selective binding of molecules to such surfaces in a chemical of physical manner. Several approaches have been made to provide compounds serving as potent candidates for the above purposes. Nevertheless the state of the art compounds do not combine all desired features as some of them are moisture sensitive, lack the possibility of being apt to be modified and therefore customized easily or suffer from drawbacks like high volume shrinkage and the like.

Japanese Patent Application No. 1999-191117 discloses primers containing heterocyclic oxathiolanethione derivatives, m-xylylenediamine, epoxy resins and neopentyl glycol diglycidyl ether, in particular for use in concrete production. Anticorrosive coating compositions with similar ingredients are described in Japanese Patent Application No. 1999-372469.

Japanese Patent Application No. 2000-234080 discloses rapidly curable, storage stable resin compositions comprising dithiocarbonates and oxazolidines and/or ketimines.

Low-temperature-curable epoxy resin compositions are reported in Japanese Patent Application No. 2001-259110. The therein disclosed compositions

comprise oxathiolanethione derivatives, polysulfide-modified epoxy resins and compounds with at least two active hydrogen atoms from amino groups.
Further epoxy resin compositions containing dithiocarbonates are described in Japanese Published Patent Application No. 2000-273150-A for use in fiber reinforced composite material and in Japanese Published Patent Application No. 2001-206934-A for use in anticorrosion coatings, exterior and car coatings, powder coatings, as primers and structural adhesives.

None of the documents discussed above describes compounds containing a dithiocarbonate group and a further reactive group, like e.g. a silyl group within one molecule.

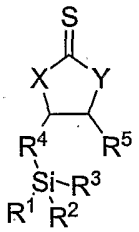
Japanese Patent Publication No. 11-246632 concerns polymeric compounds for use in paints, adhesives, inks and sealing agents, which are prepared by copolymerization of five-membered cyclic dithiocarbonates and silanes, both carrying vinyl groups as reactive groups for polymerization. The aim of JP 11-246632 is to provide surface coatings with improved hardness, as well as water and chemical resistance. Nevertheless those molecules are polymeric and limited in their ability to be selectively modified compared to single monomeric units.

One object of the present invention is to overcome the problems of the prior art compounds and to provide key intermediates that are suitable as adhesion promoters with improved volume shrinkage characteristics, enhanced corrosion resistance properties and enhanced curing abilities, the latter one being due to the presence of different crosslinking groups such as thiol or siloxy groups within one molecule.

A further object of the invention was to provide compounds that can be applied to a large variety of different surface materials before or after selective modification by reaction to form multi-crosslinked or multi-crosslinkable coatings or primers, that are free of chromium compounds.

The compounds should also be curable or crosslinkable by so-called sol-gel formation. Such sol-gels should be capable to adhere or chemically bind to metallic and non-metallic surfaces and to provide for enhanced adhesion of further adhesives to be applied. Application areas should range from treatment of surfaces such as glass and silicone wafers to metal and alloy bonding purposes or air craft paintwork. Moreover compounds should be provided that are useful in universal applications concerning surface (pre)-treatment, coating and bonding as well as adhesion promoting.

The above problems have been solved by providing a novel class of 1,3-oxathiolane-2-thione compounds (siloxy group coupled cyclic dithiocarbonates; in the following cycDTC-Si) having the following general formula:



wherein

R^1 and R^2 are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue,

R^3 is different or the same as R^1 or R^2 or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, an araliphatic or heteroaraliphatic residue or consists of one or more siloxy groups,

R^4 is a bridging group selected from the groups consisting of aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic and heteroaromatic groups and

R^5 is hydrogen, an aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic, heteroaromatic, cycloaliphatic or heterocycloaliphatic group or

R^4 and R^5 form a cycloaliphatic, cycloheteroaliphatic, aromatic or heteroaromatic residue, which is optionally substituted with an aliphatic, heteroaliphatic residue serving as a bridging group to the silicone atom and

X and Y are different and selected from oxygen and sulfur, and mixtures of such compounds.

It is preferred that the compounds of the above general formula contain a trialkoxysilyl group, i.e. that R^1, R^2 and R^3 are the same or different and each of them is a straight-chain or branched alkoxy residue with 1 to 4 carbon atoms. Even more preferred are the compounds wherein R^1, R^2 and R^3 are the same or different and wherein each of which denotes a methoxy or ethoxy residue.

The preference for trialkoxysilyl groups instead of dialkoxymonoalkylsilyl groups is due to the increased ability in sol-gel formation when using trialkoxysilyl groups.

Methoxy and ethoxy residues are preferred because of the ready commercial availability of such precursor compounds. Nevertheless further practical reasons account for the use of compounds with methoxy and ethoxy residues. In view of the sol-gel formation pot life is one crucial issue for the applicability during the coating process. If e.g. a longer pot life is desired ethoxy or even propoxy residues are preferred over methoxy residues.

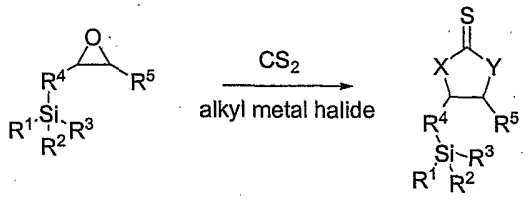
The R^4 group serves as a bridging group between the silyl group and the cyclic dithiocarbonate group. The choice of this groups is not crucial for the function of the compounds of this invention. Therefore a wide variety of residues ranging from saturated to unsaturated, straight-chain or branched residues or aromatic residues, optionally containing hetero atoms can be part of the bridging group. In general, but not limited thereto, the bridging group contains 1 to 12 atoms standing in series between the silyl and the cyclic dithiocarbonate group. One preferable meaning of R^4 is $-(CH_2)_3OCH_2-$ when R_5 is hydrogen.

R^4 can also form a ring system together with R^5. If a ring system is formed between R^4 and R^5, usually 4 to 8 atoms are involved in the ring. If e.g. a 6-membered cycloalkyl ring is formed the 1,3-oxathiolane-2-thione residue develops to a 1,3-benzoxathiole-2-thione residue at which the silyl residue can either be bound directly or via another spacer as in 2-{3,4-(1,3-oxathiolane-2-

thionyl)cyclohexyl}-ethyltriethoxysilane or 2-{4,5-(1,3-oxathiolane-2-thionyl)cyclohexyl}ethyltriethoxy-silane (see Examples; compounds 1c and 1c'), i.e. R^4 and R^5 together form $-(CH_2-CH_2-CHR^x-CH_2)-$ whereby R^x is $-CH_2-CH_2-$.

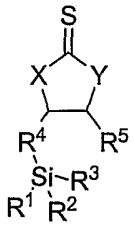
The present invention further provides a method for preparation of the 5-membered cycDTC-Si. Various cycDTC-Si compounds can be synthesized by cycloaddition of carbon disulfide with epoxy-silanes according to diagram 1:

Diagram 1



X,Y = S or O; and X not Y

With other words it is provided method for the preparation of compounds having the general of formula (I):



(I)

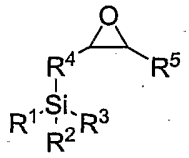
wherein

R^1 and R^2 are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue,

R^3 is different or the same as R^1 or R^2 or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, or an araliphatic or heteroaraliphatic residue,

R^4 is a bridging group selected from the groups consisting of aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic and heteroaromatic groups and

R^5 is hydrogen, an aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic, heteroaromatic, cycloaliphatic or heterocycloaliphatic group or
R_4 and R_5 form a cycloaliphatic, cycloheteroaliphatic, aromatic or heteroaromatic residue, which is optionally substituted with an aliphatic, heteroaliphatic residue serving as a bridging group to the silicone atom and
X and Y are different and selected from oxygen and sulfur, characterized in that an epoxy compound of general formula (II):



(II)

wherein R^1, R^2, R^3, R^4 and R^5 are the same as in formula (I), is brought to reaction with carbon disulfide in the presence of a catalyst.

The position at which the mandatory atoms S and O are present in the 5-membered ring – X or Y position, respectively – depends on a variety of factors like the substitution pattern at positions 4 and 5 of the 5-membered ring, the choice of catalyst, reaction conditions like temperature and the like. Nevertheless for fulfillment of the uses of the invention, both isomers are suitable.

As a catalyst, various alkali metal halides, such as chlorides, iodides and bromides of sodium, potassium and lithium can be used. Most commonly used are the iodides and bromides of sodium and lithium, whereby the most preferable one is lithium bromide in view of selectivity and yield when an ether, such as the cyclic ether tetrahydrofuran is used as a solvent. Further examples are lithium chloride, lithium iodide, sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide and potassium iodide. Other catalysts that might be employed include e.g. oxides like aluminum oxides, titanium oxides, silica, tin oxide, zinc oxide and lead(II)oxide.

The reaction can be preformed with or without solvents. As reaction media various solvents can be used instead of or in combination with ethers or cyclic ethers like

tetrahydrofuran. Possible solvents are e.g. ketones such as acetone or ethylmethylketone, amides such as dimethylformamide N-methylpyrrolidin-2-one, alcohols such as methanol, ethanol, 2-propanol, nitriles such as acetonitrile, propionitrile, as well as solvent mixtures.

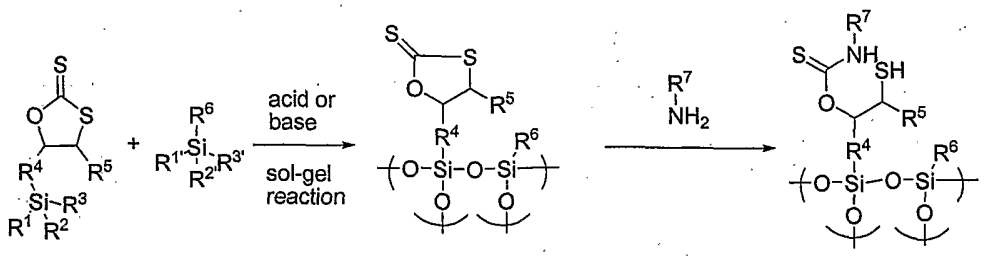
The reaction is preferably performed at a temperature of 0 to 100 °C and a pressure of 1 to 5 atmospheres. More preferably the reaction is carried out at a temperature of 0 to 50 °C and a pressure of 1 to 2 atmospheres.
The silyl group is not affected under the reaction conditions.

The compounds of the present invention are in particular useful in pre-treatment, surface coating and bonding of various metallic and non-metallic surfaces, including surfaces like aluminum, titanium, steel, gold, silver, copper, various alloys, glass, silicone in any shape from macroscopically flat surfaces to small particles.

The compounds of the present invention can easily form a solvent-resistant layer on surfaces of various materials by sol-gel reaction of the silyl part, whereby a combination with other silyl compounds is possible (see diagram 2). The conditions for sol-gel reactions are known to the skilled in the art and not deemed to limit the scope of the present invention. Usually such reactions are acid or base induced. Most commonly used acids and bases used for sol-gel formation are inorganic acids such as hydrochloric acid and sulfuric acid, organic acids such as acetic acid and p-toluenesulfonic acid, inorganic bases such as sodium hydroxide, potassium hydroxide, and ammonia, organic bases such as amines. Moreover US 5,849,110 and 5,789,085, which are included herein by reference, describe several possible mechanisms of sol-gel formation of epoxy-silanes.

When reactive groups such as hydroxy groups, amino groups, carboxy groups, thiol groups and the like are present on the surface to be treated, the layer can be covalently bound to the surface.

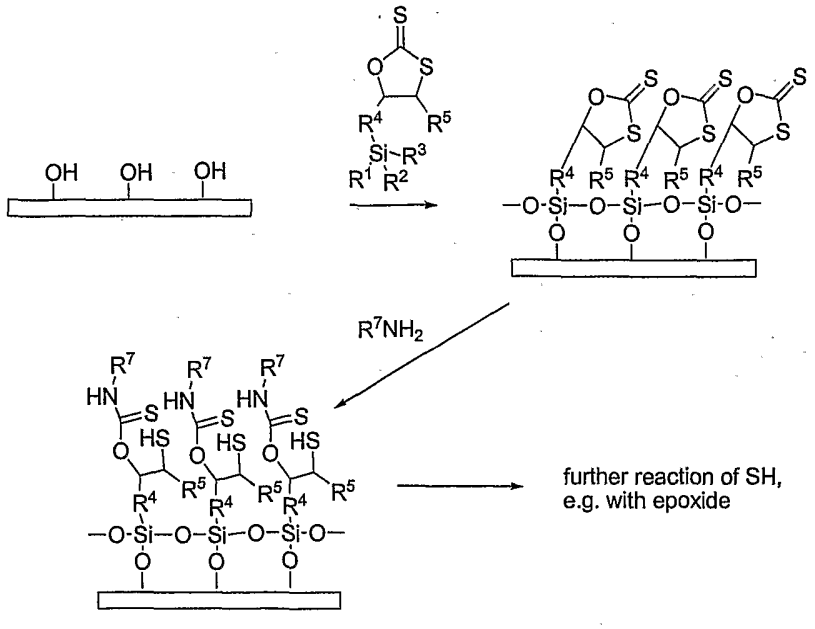
Diagram 2



Thus pre-treated (or coated) surfaces have the following features:

The pre-treated (or coated) substrate bears cyclic dithiocarbonates (cycDTC) on its surface, which can react with amines in adhesive formulations (diagram 3). By this ring cleavage reaction, thiol groups are formed. The thiol groups can further react with epoxides in the adhesive formulation. These reactions improve the resulting adhesion performance. In addition, on the pre-treated (or coated) surface, various peptides, nucleic acids, and other functional molecules can be immobilized by their reactions with cycDTC. Due to the very selective reaction of cycDTC with amines, the modified surface is relatively moisture inert or insensitive and therefore has an enhanced long-term stability compared to the conventional ones bearing epoxide and isocyanate groups at the surface.

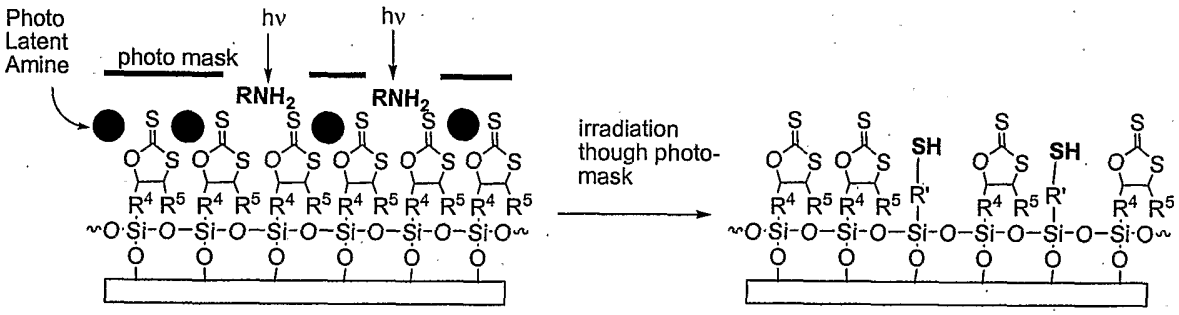
Diagram 3



Using photo-latent amines, photo-patterning can be achieved on the pre-treated surface (diagram 4). Examples of such photo-latent amines are O-acyloximes (cf. JP2002-201256). The patterned reactive surface can afterwards e.g. be used to immobilization of peptides and enzymes by the oxidative coupling of their thiol groups with the thiol group of the surface.

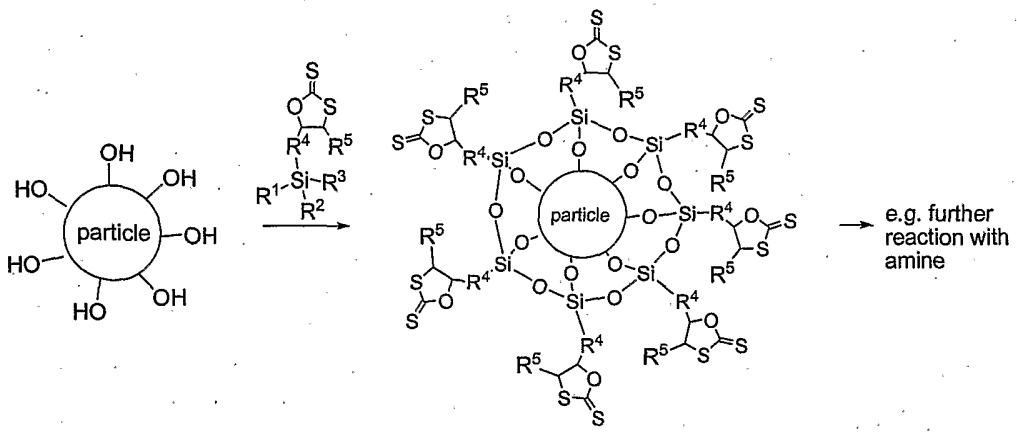
The surface thiol group can be also used for immobilization of various metal nano-particles such as gold, silver or copper, and the immobilized particles can form nano-scale circuits for nano-size electronic devices.

Diagram 4



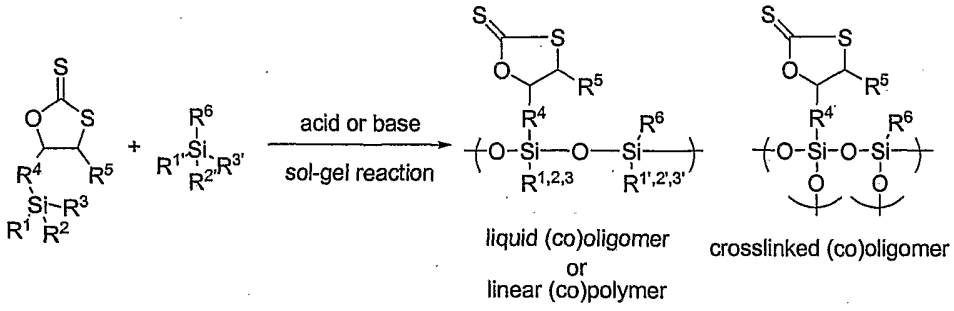
Moreover the pre-treated surfaces of particles (e.g. silica-gel particles, metal particles, and other organic and inorganic particles) bearing cycDTC, can react with amines in adhesive and sealant formulations (diagram 5). This reaction forms covalent bondings between the surface and adhesives and sealants to improve the adhesion performance, properties of adhesives and those of sealants. The particles can be used as scavengers for amines. In addition, the particles can be modified by reaction with amines, and appropriately modified ones can be used as stationary phase for column chromatography.

Diagram 5



Another field of application makes use of liquid oligosiloxanes, crosslinked polysiloxanes, and linear polysiloxanes bearing the cycDTC group (diagram 6). The sol-gel reaction of the siloxane part of cycDTC-Si polymerizes acid or base catalyzed in the presence of moisture. As catalysts, various acidic and basic reagents, which are commonly used for sol-gel reactions can be employed. Co-polymerization with other siloxanes is also possible (diagram 6), nevertheless the siloxanes described in diagram 6 can also be omitted.

Diagram 6



The crosslinked (co)oligomer is a solid (monolith or powder) and insoluble in any solvent. The cycDTC part of it can react with amines as described above. Based on this reaction, the crosslinked (co)oligomer has the same features as the surface bound analogues discussed for the pre-treatment (or coating) of materials.

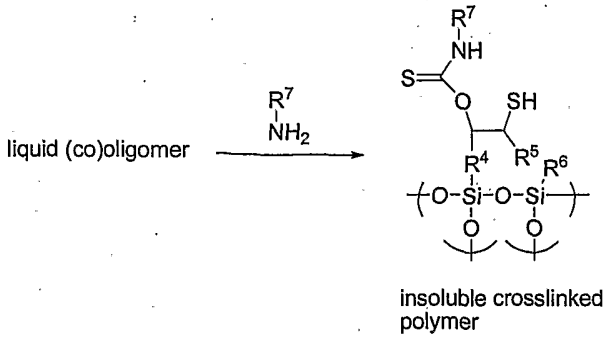
If the above reaction is carreid out in the presence of compounds of the general formula $SiR^{1'}R^{2'}R^{3'}R^{6}$, the residues would preferably denote as follows:
$R^{1'}$ and $R^{2'}$ are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue,
$R^{3'}$ is different or the same as R^{1} or R^{2} or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, or an araliphatic or heteroaraliphatic residue and
R^{6} denotes a straight-chain or branched aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic or heteroaromatic group.

By variation of the reaction time it is possible to selectively obtain liquid and solid products, respectively. A short reaction time in general leads to liquid products and longer reaction times give solid products. In most cases, but always depending on the starting materials, a 5 h reaction time leads to a liquid product. To the contrary reaction times of e.g. more than 24 h are employed if solid products should be obtained.

The liquid (co)oligomers are less volatile than monomeric cycDTC, and have higher viscosity, and therefore can be handled more easily than monomeric cycDTC. The obtained liquid (co)oligomers are soluble in organic solvents, and miscible with various organic compounds.

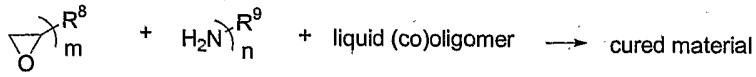
Treatment of the liquid (co)oligomers with amine results in a ring opening reaction of the cycDTC moiety in the side chain of the oligomers and post condensation reactions of the oligosiloxane part to give crosslinked polysiloxanes (diagram 7). Thus, the oligomers can be applied as curable materials to adhesives, coatings, and sealants.

Diagram 7



The liquid (co)oligomers are miscible with epoxy resins and thus can be used in addition to epoxy resins. Using the (co)oligomers as additives for epoxy-amine curing reaction (diagram 8), volume shrinkage can be reduced. Addition of monomeric cycDTC-Si itself is also possible.

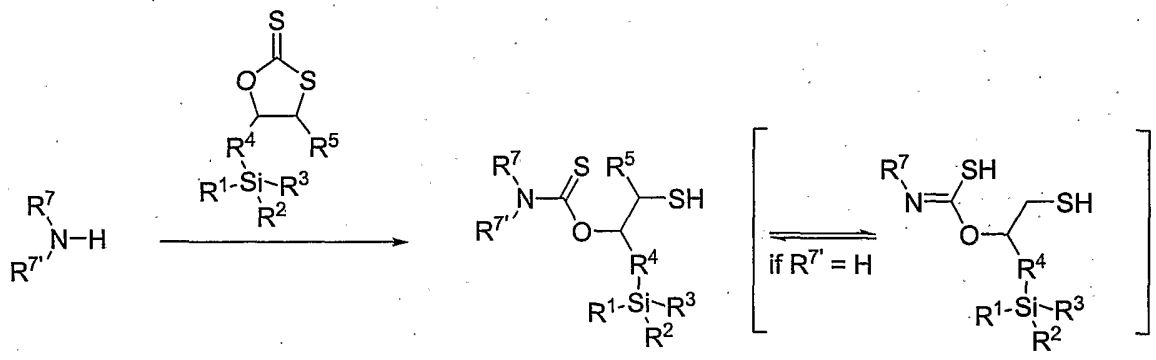
Diagram 8



Further it is possible to prepare a monomeric thiol having a siloxy moiety by reaction of an amine with cycDTC-Si (diagram 9): The cycDTC group of cycDTC-Si reacts with an amine of the formula $NHR^7R^{7'}$ or a polymeric polyamine selectively to give the corresponding thiourethane having thiol and siloxy moieties (the definition of R^1, R^2, R^3, R^4 and R^5 is as used above; and R^7 and $R^{7'}$ are the same or different and denote hydrogen, a straight-chain or branched aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic or heteroaromatic group). In case a polymeric polyamine is used, such as e.g. a polyoxyalkylene diamine or triamine with a number-average molecular weight of 200 to 5000 or preferably 200 to 1000.

By such reactions, various amines can be modified into the corresponding thiols having siloxy moieties. The thiol moiety of the adduct can e.g. be used for oxidative coupling reactions and reactions with epoxide, similar to the other thiols as described above.

Diagram 9



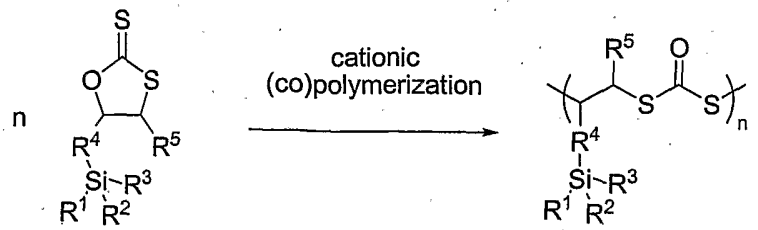
The thus modified amines can be used for pre-treatment and coating of surfaces of various materials by sol-gel reaction of the siloxy group. The resulting coating layer has thiol groups, which can e.g. react with epoxides, isocyanates, isothiocyanates, thiols, and carboxylic acid derivatives, improving adhesion performance. The physical properties of the coating layer can be controlled by choosing the starting amine.

Furthermore the modified amine can be used as a curable material. Sol-gel reaction of siloxy part and oxidative coupling of thiol group results in a strong curing reaction with a high degree of crosslinking.

Another use of such modified amines is the use as a curing reagent for epoxy and urethane adhesives, coatings, and sealants. The siloxy part enhances adhesion performance and increases mechanical strength of the cured material. The thiol group promises rapid curing reaction.

Apart from the polymerization of the siloxy group by sol-gel formation a polymerization of cycDTC-Si induced by cationic initiators such as trifluoromethane sulfonic acid alkyl esters, alkyl triflates, Lewis acids or tin tetrachloride, or photo latent initiators such as diaryliodonium salt, can be performed to give the corresponding polymer having siloxy moieties in the side chain, which are also compounds of the present invention (diagram 10).

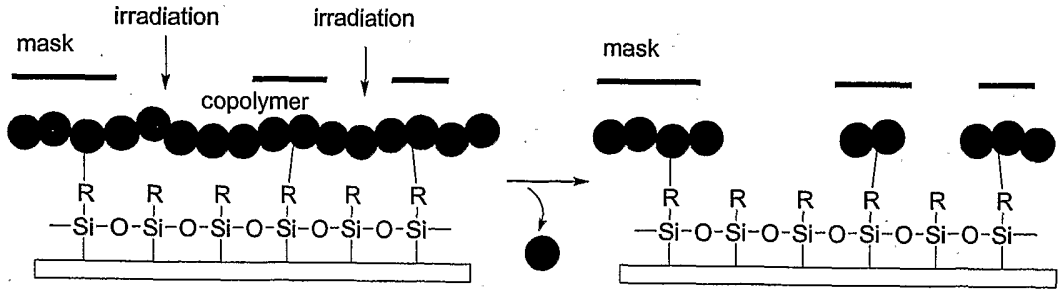
Diagram 10



$n \approx 2$ to 1000

The main chain is consisting of a poly(dithiocarbonate), which has a high reflective index. The polymer can be cured by sol-gel reaction of the siloxy moiety in the side chain. The obtained cured material or cured coating layers can be used as optical materials. In addition, based on the possible irradiation caused depolymerization of poly(dithiocarbonate), micropatterns can be fabricated on material surfaces using masks that only partially cover the coated substrate surface (diagram 11). Such micropatterns can be employed in photo-electronics devices such as photo-circuits.

Diagram 11



Any of the compounds or sol-gels of the invention described for use in adhesive formulations and sealant compositions are preferably used in a concentration of up to 20 wt.-%, more preferably 0.1 to 10 wt.-% and most preferably 1 to 5 wt.-%, based on the total weight of the adhesive or sealant composition.

PREPARATION EXAMPLES

If not otherwise specified, all reagents and solvents were used as purchased. Silanes having a epoxy moiety were purchased from Shin-etsu Chemical Co., Ltd. Other reagents were purchased from Wako Chemical Co., Ltd. Solution NMR spectra (400 MHz ^{1}H, δ_{CHCl3} = 7.26 ppm; 100.6 MHz ^{13}C, δ_{CHCl3} = 77.00 ppm; 79.5 MHz ^{29}Si, δ_{TMS} = 0.00 ppm) were obtained on a Varian NMR spectrometer model Unity INOVA. Solid-state NMR spectra (100.6 MHz ^{13}C, δ_{TMS} = 0.00 ppm; 79.5 MHz ^{29}Si, δ_{TMS} = 0.00 ppm) were obtained on a Bruker NMR spectrometer model DSX400 by use of HPDEC (dipole decoupling) method. IR spectra were obtained on a JASCO FT/IR-460 plus. Number average molecular weight (M_n) and weight average molecular weight (M_w) were estimated from size exclusion chromatography (SEC), performed on a Tosoh chromatograph model HLC-8120GPC equipped with Tosoh TSK gel-SuperHM-H styrogel columns molecular weight analysis (6.0 mm ϕ x 15 cm), using tetrahydrofuran as an eluent at the flow rate of 0.6 mL/min after calibration with polystyrene standards. SEM-image and elemental analysis data were obtained using SEM/EDX (Hitachi SEM/EDX III typeN, Horiba EX-7000) at an accelerating voltage of 25 kV, and the sample was not sputter-coated.

Preparation of cycDTC-Si of the invention

The synthetic route for the preparation of different cycDTC-Si is shown in Schemes 1 and 2.

To a solution of (3-glycidoxypropyl)trimethoxy-silane (X=methoxy; 75.6 g, 320 mmol) and lithium bromide (1.38 g, 16.0 mmol) in tetrahydrofuran (250 ml), a solution of carbon disulfide (29.2 g, 384 mmol) in tetrahydrofuran (150 ml) was added dropwise at 0 °C, and the mixture was stirred at 25 °C. After 12 h, the volatiles were removed under reduced pressure, and the residue was dissolved in diethylether (500 ml), washed with saturated distilled water (200 ml) three times. The ether layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was distilled under vacuum to give 5-(3-

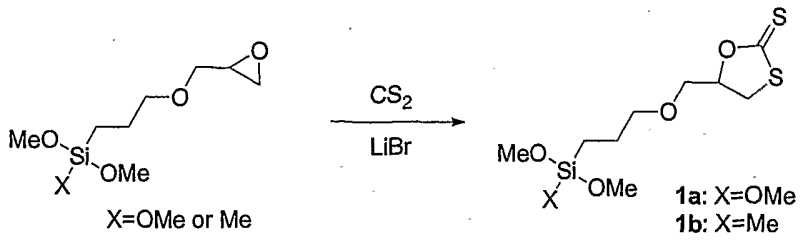
trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione (**1a**) as a yellow oil (51.2 g, 164 mmol, 51%).

$Bp_{0.34}$ = 164 °C; ^{1}H-NMR ($CDCl_3$, 20 °C) 5.23 (m, 1H, -CH_2-C<u>H</u>(-O-)-CH_2-), 3.80 and 3.73 (two dd, 2H, -S-C<u>H_2</u>-CH(-O-)-), 3.69 and 3.60 (two dd, 2H, -CH(-O-)-C<u>H_2</u>-O-), 3.58 (s, 9H, -Si-(OC<u>H_3</u>)$_3$), 3.53 (t, 2H, -O-C<u>H_2</u>-CH_2-), 1.68 (m, 2H, -CH_2-C<u>H_2</u>-CH_2-), 0.67 (m, 2H, -CH_2-C<u>H_2</u>-Si-) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 211.9 (-S-<u>C</u>(=S)-O-), 89.2 (-CH_2-<u>C</u>H(-O-)-CH_2-), 73.8 (-O-<u>C</u>H_2-CH_2-), 69.1 (-CH(-O-)-<u>C</u>H_2-O-), 50.4 (-Si-(O-<u>C</u>H_3)$_3$), 36.0 (-S-<u>C</u>H_2-CH(-O-)-), 22.6 (-CH_2-<u>C</u>H_2-CH_2-), 5.0 (-CH_2-<u>C</u>H_2-Si-) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –42.0 ppm; IR (neat) 2941, 2840, 1456, 1440, 1346, 1231, 1192, 1080, 821 cm^{-1}.

By a similar procedure, from (3-glycidoxypropyl)dimethoxymethylsilane (X=Me) (10.0 g, 45.5 mmol), 5-[3-(dimethoxymethysilyl)propyloxymethyl]-1,3-oxathiolane-2-thione (**1b**) was obtained (11.0 g, 37.2 mmol, 82 %).

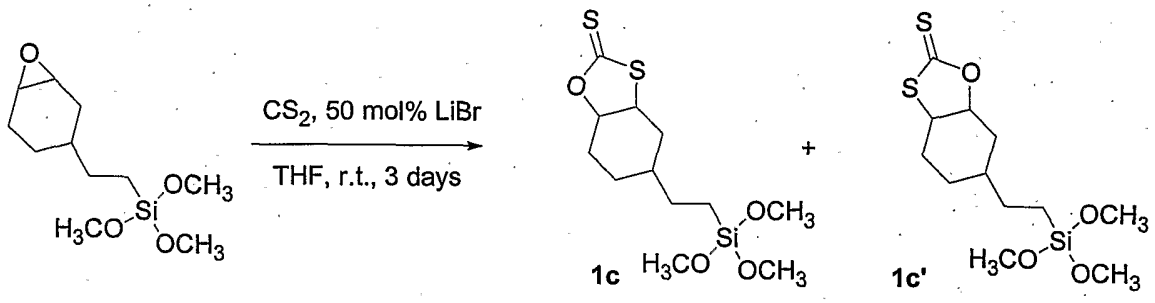
$Bp_{0.22}$ = 155 °C; ^{1}H-NMR ($CDCl_3$, 20 °C) 5.23 (m, 1H, -CH_2-C<u>H</u>(-O-)-CH_2-), 3.81 and 3.75 (two dd, 2H, -S-C<u>H_2</u>-CH(-O-)-), 3.70 and 3.61 (two dd, 2H, -CH(-O-)-C<u>H_2</u>-O-), 3.52 (s, 6H, -Si-(OC<u>H_3</u>)$_2$), 3.51 (t, 2H, -O-C<u>H_2</u>-CH_2-), 1.66 (m, 2H, -CH_2-C<u>H_2</u>-CH_2-), 0.65 (m, 2H, -CH_2-C<u>H_2</u>-Si-), 0.13 (s, 3H, -Si-C<u>H_3</u>) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 211.8 (-S-<u>C</u>(=S)-O-), 89.2 (-CH_2-<u>C</u>H(-O-)-CH_2-), 73.8 (-O-<u>C</u>H_2-CH_2-), 69.0 (-CH(-O-)-<u>C</u>H_2-O-), 49.9 (-Si-O-(<u>C</u>H_3)$_2$), 35.8 (-S-<u>C</u>H_2-CH(-O-)-), 22.5 (-CH_2-<u>C</u>H_2-CH_2-), 8.8 (-CH_2-<u>C</u>H_2-Si-), –6.1 (-Si-<u>C</u>H_3) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –1.4 ppm; IR (neat) 2937, 2870, 2834, 1455, 1440, 1346, 1259, 1231, 1192, 1085, 838, 802, 769 cm^{-1}.

Scheme 1



The dithiocarbonate **1c** (obtained as a mixture with the corresponding isomer **1c'**) can be synthesized similarly, as shown in Scheme 2.

Scheme 2



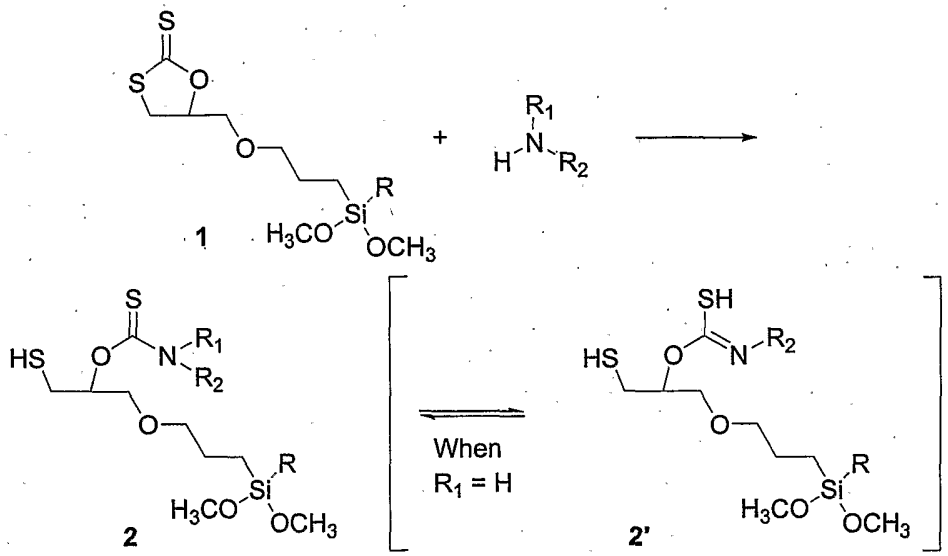
A solution of carbon disulfide (1.97 g, 29.3 mmol) in tetrahydrofuran (20 ml) was added dropwise to a mixture of 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane (EETS) (5.12 g, 20.8 mmol) and lithium bromide (0.907 g, 10.4 mmol) in tetrahydrofuran (40 ml) at room temperature for 1 hour. The resulting mixture was stirred at room temperature for 3 days. After the volatiles were removed under reduced pressure, the residue was dissolved in diethylether (50 ml). The solution was washed with saturated $NaCl_{(aq)}$ (100 ml) and distilled water (100 ml), and the obtained organic layer was dried over magnesium sulfate over night. The solution was filtrated and concentrated under reduced pressure, and the residue was dissolved in chloroform (15 ml), and was fractionated by preparative GPC to give a mixture of 2-{3,4-(1,3-oxathiolane-2-thionyl)cyclohexyl}-ethyltriethoxysilane (**1c**) and 2-{4,5-(1,3-oxathiolane-2-thionyl)cyclohexyl}-ethyltriethoxysilane (**1c'**) as a yellow oil (1.37 g, 4.36 mmol, 21 %).

The ratio **1c** : **1c'** was found to be 1 : 1 by ^{1}H-NMR analysis of the mixture: ^{1}H-NMR ($CDCl_3$, 20 °C) 4.48 (two t), 4.35-4.22 (m), 4.05 (two t), 3.88 (two t), 3.74-3.52 (m), 3.30-3.11 (m), 2.41-0.82 (m), 0.69-0.61 (m) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 212.4 and 212.2 (-S-C(=S)-O-), 126.9 and 126.4 (-CH(-S-)-CH(-O-)-CH_2-), 53.1, 52.6, 51.8, 51.7, 50.5 and 50.4 (-Si-O-(CH_3)$_3$), 36.7, 36.0, 35.7, 35.1, 32.9, 32.6, 32.1, 31.3, 31.2, 30.2, 29.3, 28.8, 28.7, 26.5, 25.2, 25.2, 23.9, 23.4, 6.1 and 6.0 (-CH_2-CH_2-Si-) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –41.0, –41.4, –41.4, –42.6 ppm; IR (neat) 2938, 2839, 2871, 1746, 1455, 1411, 1339, 1276, 1248, 1196, 1085, 1005, 973, 885, 804, 657 cm^{-1}.

Ring opening of cycDTC-Si with amines

1 reacts with amines to modify them into the corresponding thiols (Scheme 3). The siloxy group was not affected by the reaction.

Scheme 3



Reaction of 1 with diethylamine

Diethylamine (1.05 g, 14.3 mmol) was added to **1a** (0.855 g, 2.74 mmol) at room temperature, and the resulting mixture was stirred at room temperature for 10 minutes. An excess diethylamine was removed under reduced pressure to give **2a** (R=methoxy, R_1=R_2=ethyl; 0.898 g, 2.33 mmol, 85 %) as an yellow oil.
^{1}H-NMR ($CDCl_3$, 20 °C): 5.63 (m, 1H, -CH_2-C<u>H</u>(-O-)-CH_2-), 3.82 (q, 2H, -N-C<u>H_2</u>-CH_3), 3.78 and 3.68 (two dd, 2H, -CH(-O-)-C<u>H_2</u>-O-), 3.57 (s, 9H, -Si-(OC<u>H_3</u>)$_3$), 3.50-3.43 (m, 4H, -N-C<u>H_2</u>-CH_3 and -O-C<u>H_2</u>-CH_2-), 2.92 (m, 2H, -CH(-O-)-C<u>H_2</u>-SH), 1.71-1.62 (m, 2H, -CH_2-C<u>H_2</u>-CH_2-), 1.44 (t, 1H, -CH_2-S<u>H</u>), 1.25 (t, 3H, -N-CH_2-C<u>H_3</u>), 1.18 (t, 3H, -N-CH_2-C<u>H_3</u>), 0.69-0.66 (m, 2H, -CH_2-C<u>H_2</u>-Si-) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 186.0 (-O-<u>C</u>(=S)-N-), 79.0 (-CH_2-<u>C</u>H(-O-)-CH_2-), 73.2 (-O-<u>C</u>H_2-CH_2-), 68.9 (-CH(-O-)-<u>C</u>H_2-O-), 50.3 (-Si-(O<u>C</u>H_3)$_3$), 47.7 and 43.4 (-N-<u>C</u>H_2-CH_3), 24.7 (-CH(-O-)-<u>C</u>H_2-SH), 22.6 (-CH_2-<u>C</u>H_2-CH_2-), 13.1 and 11.7 (-N-CH_2-<u>C</u>H_3), 5.1 (-CH_2-

$C\underline{H_2}$-Si-) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –41.7 ppm; IR (neat) 2972, 2940, 2871, 2840, 2556(SH), 1506, 1429, 1316, 1283, 1244, 1174, 1087, 821, 792 cm^{-1}.

A similar reaction of **1b** (0.526 g, 1.77 mmol) with diethylamine (0.667 g, 9.12 mmol) gave **2b** (R=methyl, R_1=R_2=ethyl; 0.523 g, 1.42 mmol, 80 %).
^{1}H-NMR ($CDCl_3$, 20 °C) 5.63 (m, 1H, -CH_2-C$\underline{H}$(-O-)-CH_2-), 3.82 (q, 2H, -N-C$\underline{H_2}$-CH_3), 3.77 and 3.68 (two dd, 2H, -CH(-O-)-C$\underline{H_2}$-O-), 3.52 (s, 6H, -Si-(OC$\underline{H_3}$)$_2$), 3.50-3.42 (m, 4H, -N-C$\underline{H_2}$-CH_3 and -O-C$\underline{H_2}$-CH_2-), 2.92 (m, 2H, -CH(-O-)-C$\underline{H_2}$-SH), 1.67-1.59 (m, 2H, -CH_2-C$\underline{H_2}$-CH_2-), 1.44 (t, 1H, -CH_2-S$\underline{H}$), 1.25 (t, 3H, -N-CH_2-C$\underline{H_3}$), 1.19 (t, 3H, -N-CH_2-C$\underline{H_3}$), 0.65-0.61 (m, 2H, -CH_2-C$\underline{H_2}$-Si-), 0.12 (s, 3H, -Si-C$\underline{H_3}$); ^{13}C-NMR ($CDCl_3$, 20 °C) 186.0 (-O-$\underline{C}$(=S)-N-), 79.0 (-CH_2-$\underline{C}$H(-O-)-CH_2-), 73.5 (-O-$\underline{C}H_2$-CH_2-), 68.9 (-CH(-O-)-$\underline{C}H_2$-O-), 50.0 (-Si-(O$\underline{C}H_3$)$_2$), 47.7 and 43.3 (-N-$\underline{C}H_2$-CH_3), 24.7 (-CH(-O-)-$\underline{C}H_2$-SH), 22.7 (-CH_2-$\underline{C}H_2$-CH_2-), 13.1 and 11.7 (-N-CH_2-$\underline{C}H_3$), 8.9 (-CH_2-C$\underline{H_2}$-Si), –6.0 (-Si-$\underline{C}H_3$) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –1.24 ppm; IR (neat) 2972, 2936, 2871, 2834, 2551(SH), 1508, 1429, 1350, 1317, 1283, 1244, 1173, 1086, 837, 801, 769 cm^{-1}.

Reaction of 1a with benzylamine

Benzylamine (0.205 g, 1.91 mmol) was added to **1a** (0.626 g, 2.00 mmol) at room temperature, and the resulting mixture was stirred at room temperature for 10 minutes. The resulting product was dissolved in tetrahydrofuran (10 ml), and poured into hexane (200 ml) to obtain a mixture of the corresponding adduct **2c** (R=methoxy, R_1=H, R_2=CH_2Phenyl) and the corresponding tautomer **2c'** (R=methoxy, R_2=CH_2Phenyl) as an oil (0.711 g, 86 %).
IR (neat) 3268 (NH), 3030, 2941, 2840, 2568 (SH), 1742, 1658, 1524, 1455, 1401, 1344, 1247, 1182, 1079, 820, 699 cm^{-1}; ^{29}Si-NMR ($CDCl_3$, 20 °C) –41.7, –41.8 ppm;
2c: ^{1}H-NMR ($CDCl_3$, 20 °C): 7.38-7.25 (m, $C_6\underline{H_5}$), 6.72 (m, -C(=S)-N$\underline{H}$-CH_2- of adduct), 5.60-5.57 (m, -CH_2-C$\underline{H}$(-O-)-CH_2-), 4.76-4.73 (m, -NH-C$\underline{H_2}$-Ph), 3.82-3.62 (m), 3.56 (s, -Si-(OC$\underline{H_3}$)$_3$ of adduct), 3.49-3.42 (m), 2.91-2.88 (m, -CH(-O-)-C$\underline{H_2}$-SH), 1.72-1.60 (m, -CH_2-C$\underline{H_2}$-CH_2-), 1.49 (t, -CH_2-S$\underline{H}$ of adduct), 0.69-0.64 (m, -CH_2-C$\underline{H_2}$-Si-) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 189.3 (-O-$\underline{C}$(=S)-N- of adduct), 136.4

(*ipso-Ph* of adduct), 128.3 (*m-Ph* of tautomer), 128.3 (*m-Ph* of adduct), 127.4, 127.3, 127.3, 127.2 (*o-Ph* and *p-Ph*), 80.1 (tautomer), 78.7 (adduct), 74.8, 73.4, 73.4, 72.7, 68.7, 68.6, 48.8, 31.9, 24.3, 23.4, 22.4, 22.3, 4.81, 4.79 ppm.

2c': This tautomer was distinguished from **2c** by the following signals in ^{1}H-NMR spectrum of the mixture: ^{1}H-NMR ($CDCl_3$, 20 °C) 6.94 (m, -N=C-S*H* of tautomer), 3.57 (s, -Si-(OC*H*$_3$)$_3$ of tautomer), 1.34 (t, -CH_2-S*H* of tautomer), ^{13}C-NMR ($CDCl_3$, 20 °C): 188.3 (-O-*C*(-SH)=N- of tautomer), 136.6 (*ipso-Ph* of tautomer).

Reaction of 1a with dibenzylamine

Dibenzylamine (2.28 g, 11.6 mmol) was added to **1a** (0.750 g, 2.00 mmol) at room temperature, and the resulting mixture was stirred at room temperature for 15 hours. The conversion was estimated at 52 % by ^{1}H-NMR analysis. By ^{1}H-NMR analysis of the mixture, formation of the corresponding adduct **2d** (R=methoxy, R_1=R_2=CH_2Phenyl) was confirmed.

^{1}H-NMR ($CDCl_3$, 20 °C): 7.39-7.17 (m, C_6H_5), 5.74-5.72 (m, -CH_2-C*H*(-O-)-CH_2-), 5.13 (s, -N-C*H*$_2$-Ph), 4.68-4.57 (dd, -N-C*H*$_2$-Ph), 3.82-3.56 (m), 3.55 (s, -Si-(OC*H*$_3$)$_3$), 3.54-3.39 (m), 2.92-2.86 (m, -CH(-O-)-C*H*$_2$-SH), 1.74-1.64 (m, -CH_2-C*H*$_2$-CH_2-), 1.34 (t, -CH_2-S*H*), 0.69-0.62 (m, -CH_2-C*H*$_2$-Si-) ppm.

Reactions of the thiol moiety after cleavage of cycDTC-Si

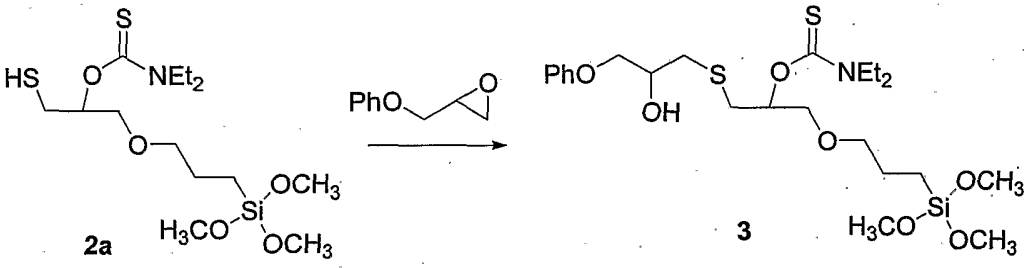
Reaction of the thiol group with epoxide

A mixture of glycidyl phenyl ether (0.650 g, 4.33 mmol) and **2a**, prepared from **1a** (1.25 g, 4.01 mmol) and diethylamine (1.44 g 19.6 mmol), was stirred at room temperature for 6 days (Scheme 4). Complete consumption of **2a** was confirmed by ^{1}H-NMR analysis. The resulting product was dissolved in tetrahydrofuran (20 ml), and poured into hexane (200 ml) to obtain the crude product as an oil, which was fractionated by preparative GPC to obtain 3-(3-phenoxy-2-hydroxypropyloxy)-2-(N,N-diethylthioureoxy)-1-(3-trimethoxy-silylpropyloxy)propane (**3**) (0.345 g, 0.644 mmol, 16 %).

^{1}H-NMR ($CDCl_3$, 20 °C). 7.28 (t, 2H, Ph(*m-H*)), 6.96 (t, 1H, Ph(*p-H*)), 6.92 (d, 2H, Ph(*o-H*)), 5.75-5.68 (m, 1H, -CH_2-C*H*(-O-)-CH_2-), 4.20-4.13 (m, 1H, -CH_2-C*H*(OH)-

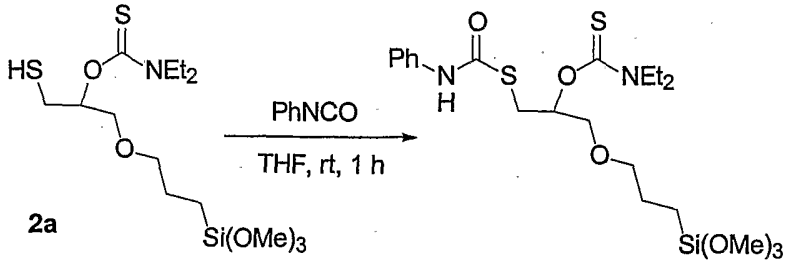
CH_2-), 4.08-3.66 (m, 6H, -N-C$\underline{H_2}$-CH_3, -CH(-O-)-C$\underline{H_2}$-O-, -CH(-OH)-C$\underline{H_2}$-O-), 3.56 (s, 9H, -Si-(OC$\underline{H_3}$)$_3$), 3.52-3.38 (m, 4H, -N-C$\underline{H_2}$-CH_3 and -O-C$\underline{H_2}$-CH_2-), 3.06-2.76 (m, 4H, -CH(-O-)-C$\underline{H_2}$-S- and -CH(-OH)-C$\underline{H_2}$-S-), 1.71-1.63 (m, 2H, -CH_2-C$\underline{H_2}$-CH_2-), 1.24 (t, 3H, -N-CH_2-C$\underline{H_3}$), 1.17 (t, 3H, -N-CH_2-C$\underline{H_3}$), 0.68-0.64 (m, 2H, -CH_2-C$\underline{H_2}$-Si-) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 186.1 (-O-$\underline{C}$(=S)-N-), 158.4 (Ph(*ipso*-$\underline{C}$)), 129.4 (Ph(*m*-$\underline{C}$)), 121.0 (Ph(*p*-$\underline{C}$)), 114.5 (Ph(*o*-$\underline{C}$)), 77.9 and 77.8 (-CH_2-$\underline{C}$H(-O-)-CH_2-) 73.3 (-O-$\underline{C}H_2$-CH_2-), 70.3 and 70.2 (-CH(-O-)-$\underline{C}H_2$-O-), 69.7 and 69.6(-CH(-OH)-$\underline{C}H_2$-O-), 68.8 and 67.9 (-CH_2-$\underline{C}$H(-OH)-CH_2-), 50.4 (-Si-(O$\underline{C}H_3$)$_3$), 47.8 and 43.4(-N-$\underline{C}H_2$-CH_3), 36.1 and 36.0 (-CH(-O-)-$\underline{C}H_2$-S-), 22.7 (-CH_2-$\underline{C}H_2$-CH_2-), 13.2 and 11.8 (-N-CH_2-$\underline{C}H_3$), 5.1 (-CH_2-C$\underline{H_2}$-Si-) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –41.7 ppm; IR (neat) 3409 (OH), 3060, 2966, 2940, 2872, 2839, 1651, 1599, 1587, 1506, 1457, 1430, 1379, 1362, 1350, 1316, 1284, 1245, 1173, 1084, 917, 819, 792, 756, 692 cm^{-1}.

Scheme 4



Reaction of the thiol group with isocyanate

Scheme 4'



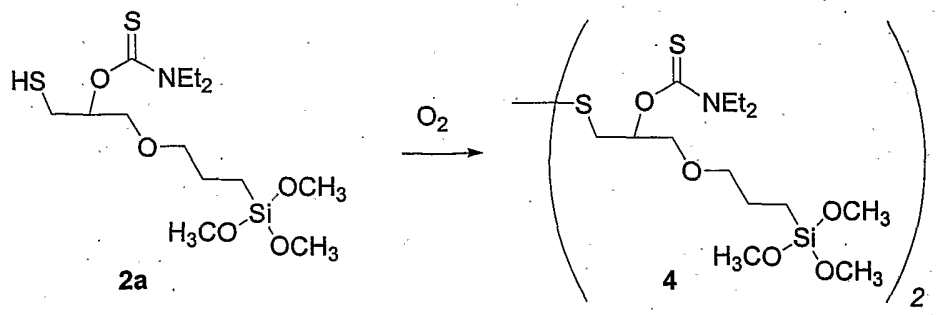
A mixture of phenyl isocyanate (142 mg, 1.19 mmol) and **2a**, prepared from **1a** (321 mg, 1.03 mmol and diethylamine (358 mg, 4.89 mmol), was stirred at room temperature for 1 hour to obtain the corresponding adduct quantitatively: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.43-7.08 (m, *Ph* and -C(=O)-N*H*-Ph, 6H), 5.83-5.77 (m, -CH_2-C*H*(-O-)-CH_2-, 1H), 3.81 (q, -N-C*H*$_2$-CH_3, 2H), 3.76-3.66 (dd, -CH(-O-)-C*H*$_2$-O-, 2H), 3.57 (s, Si-OC*H*$_3$, 9H), 3.52-3.38 (m, 6H), 1.71-1.65 (m, -CH_2-C*H*$_2$-CH_2-, 2H), 1.23 and 1.15 (t, 6H, -CH_2-C*H*$_3$), 0.69-0.65 (m, -CH_2-C*H*$_2$-Si-, 2H).

Oxidative coupling reaction between two thiol groups

The oxidative coupling reaction of the thiol group of **2a** gave the corresponding disulfide (Scheme 5): **2a**, prepared from **1a** (1.89 g, 6.05 mmol) and diethylamine (2.38 g 32.5 mmol) by the above-mentioned method, was stirred at room temperature under oxygen atmosphere for 8 days. The conversion of **2a** was estimated to be 68 % by ^{1}H-NMR analysis. Fractionation of the crude mixture by preparative GPC gave bis{3-(3-trimethoxysilylpropyloxy)-2-(N,N-diethylthioureoxy)-propane} disulfide (**4**) (0.078 g, 0.100 mmol, 3 %).

^{1}H-NMR ($CDCl_3$, 20 °C): 5.85-5.79 (m, 2H, -CH_2-C*H*(-O-)-CH_2-), 3.83-3.72 (m, 8H, -N-C*H*$_2$-CH_3 and -CH(-O-)-C*H*$_2$-O-), 3.57 (s, 18H, -Si-(OC*H*$_3$)$_3$), 3.50-3.43 (m, 8H, -N-C*H*$_2$-CH_3 and -O-C*H*$_2$-CH_2-), 3.16-3.14 (m, 4H, -CH(-O-)-C*H*$_2$-S-), 1.69-1.62 (m, 4H, -CH_2-C*H*$_2$-CH_2-), 1.23 (two t, 6H, -N-CH_2-C*H*$_3$), 1.17 (two t, 6H, -N-CH_2-C*H*$_3$), 0.67-0.63 (m, 4H, -CH_2-C*H*$_2$-Si-) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 186.1 (-O-*C*(=S)-N-), 77.4 (-CH_2-*C*H(-O-)-CH_2-), 73.4 (-O-*C*H_2-CH_2-), 69.9 and 69.8 (-CH(-O-)-*C*H_2-O-), 50.5 (-Si-(O*C*H_3)$_3$), 47.8 and 43.5 (-N-*C*H_2-CH_3), 39.6 and 39.5 (-CH(-O-)-*C*H_2-S-), 22.7 (-CH_2-*C*H_2-CH_2-), 13.3 and 11.9 (-N-CH_2-*C*H_3), 5.2 (-CH_2-C*H*$_2$-Si-) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –41.7 ppm; IR (neat) 2966, 2939, 2872, 2839, 1507, 1429, 1316, 1283, 1245, 1173, 1087, 820, 792 cm^{-1}.

Scheme 5



Sol-gel formation of the siloxy moieties after ring-opening of cycDTC-Si

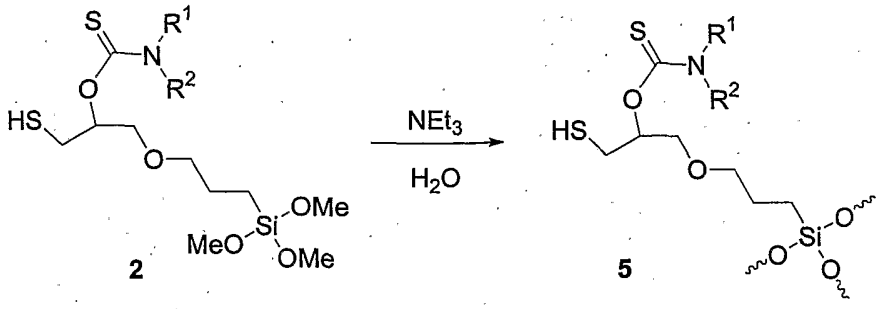
The siloxy moiety of **2** can be applied to sol-gel reaction (Scheme 6): Triethylamine (5.00 mg, 0.049 mmol) and water (37.6 mg, 2.09 mmol) were added to **2a** (0.530 g, 1.37 mmol), and the resulting mixture was stirred at room temperature for 1 day. After volatiles were removed under reduced pressure, the residue was washed with tetrahydrofuran (100 ml) to obtain **5a** (0.199 g, 38 %) as tetrahydrofuran-insoluble parts.

^{13}C-NMR (solid-state (HPDEC), 20 °C) 188.5- 186.4 (-O-C(=S)-N-), 175.4-165.5, 76.6-68.4, 58.7-30.3, 29.5-20.8, 19.6-5.5 ppm; ^{29}Si-NMR (solid-state (HPDEC), 20 °C) –65.5- –71.8 ppm; IR (KBr) 3445 (OH and NH), 2976, 2933, 2879, 2523 (SH), 1734, 1653, 1559, 1507, 1429, 1362, 1317, 1284, 1245, 1173, 1096, 1063, 1004, 800 cm^{-1}.

A similar reaction of **2b** gave the corresponding insoluble product **5b**.

^{13}C-NMR (solid-state (HPDEC), 20 °C) 188.5- 170.0 (-O-C(=S)-N- and -O-C(-SH)=N), 138.6-130.0, 124.4-118.3, 108.2-100.5, 77.6-61.6, 51.4-48.7, 48.6-23.3, 22.6-14.1, 9.6- –0.7 ppm; ^{29}Si-NMR (solid-state (HPDEC), 20 °C) –68.6- –79.4 ppm; IR (KBr) 3295 (NH), 3033, 2930, 2867, 2606 (SH), 1735, 1653, 1550, 1502, 1455, 1416, 1346, 1269, 1215, 1181, 1104 1029, 738, 721, 695 cm^{-1}.

Scheme 6



Synthesis of oligosiloxanes, crosslinked polysiloxanes and linear polysiloxanes comprising the cyclic dithiocarbonate group

Synthesis of liquid oligomers

Hydrogen chloride diethyl ether complex (HCl/diethylether, 1M in ether, 0.15 ml, 0.15 mmol) was added to mixture of **1a** (0.722 g, 2.47 mmol) and distilled water (0.0660 g, 3.67 mmol) at room temperature. After the resulting mixture was stirred at room temperature for 5 hours, volatiles were removed under the reduced pressure. The residue was dissolved in THF (30 mL), and poured into hexane (400 mL). Liquid oligomers (diagram 6) (0.661 g) with M_n = 320, M_w = 1620, and PDI = 5.1 were isolated as an yellow oil.

The similar reaction of **1a** (3.58 g, 11.4 mmol) and distilled water (0.311 g, 17.3 mmol) in the presence of triethylamine (0.0568 g, 0.561 mmol) for 5 h gave the corresponding liquid oligomers (3.28 g, M_n = 400, M_w = 1150, and PDI = 2.9).

The similar reaction of **1a** (0.724 g, 2.32 mmol) and distilled water (0.065 g, 3.61 mmol) in the presence of CH_3COOH (0.0085 g, 0.142 mmol) for 3 days gave the corresponding liquid oligomers (0.699 g, M_n = 530, M_w = 640, and PDI = 1.2).

Spectral data:

^{1}H-NMR ($CDCl_3$, 20 °C) 5.28 (br, -CH_2-C<u>H</u>(-O-)-CH_2-), 3.82-3.68 (br), 3.54 (br), 3.48 (s -Si-OC<u>H_3</u>), 1.71 (br, -CH_2-C<u>H_2</u>-CH_2-), 0.70 (br, -CH_2-C<u>H_2</u>-Si-) ppm.

^{13}C-NMR ($CDCl_3$, 20 °C) 212.3 (br, -S-C(=S)-O-), 89.6 (br, -CH_2-CH(-O-)-CH_2-), 73.9 (br, -O-CH_2-CH_2-), 69.5 (br, -CH(-O-)-CH_2-O-CH_2-), 50.9 (small, -Si-OCH_3), 36.0 (-S-CH_2-CH(-O-)-), 23.0 (-CH_2-CH_2-CH_2-), 8.6 (-CH_2-CH_2-Si-) ppm.
^{29}Si-NMR ($CDCl_3$, 20 °C) –50.3 ((CH_3O-)$_2$Si(-O-)(-CH_2-)), –59.3 (CH_3O-)Si(-O-)$_2$(-CH_2-)), –67.9 (-CH_2-)Si(-O-)$_3$) ppm.
IR(neat): 3427, 2932, 2868, 2810, 1731, 1650, 1439, 1410 1036, 903, 838, 762 cm^{-1}.

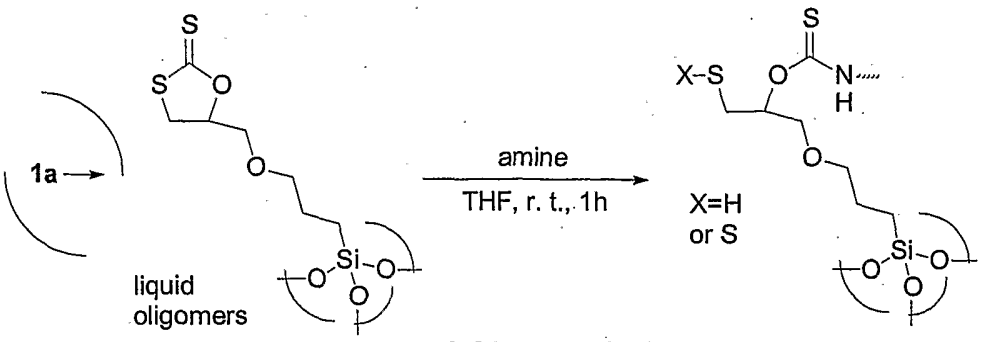
In the ^{1}H-NMR spectrum, a broad signal at 5.28 ppm assigned to -S-CH_2-CH(-O-)- in DTC structure was observed. A broad signal at 212.3 ppm assigned to -C(=S)- was confirmed by the ^{13}C-NMR spectrum. In the ^{29}Si-NMR spectrum, a signal at –42.0 ppm attributed to **1a** was disappeared. Thus, the sol-gel condensation proceeded without damaging the DTC moiety.

Post curing of liquid oligomer

The liquid oligomer (1.0 g), obtained by oligomerization of DTC-silane **1a**, was dissolved in THF (10 mL), and was casted on a silicate glass and heated at 80 °C for 24 hours. The resulting layer, immobilized on the glass surface, was insoluble in THF, chloroform, and DMF.

Reaction of the liquid oligomer with amine.

Reaction with butylamine



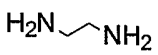
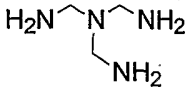
S-S bond can be formed by oxidative coupling of the thiol group, as shown in Scheme 5

To a solution of the liquid oligomer (0.271 g, 0.867 mmol (DTC unit)) (prepared from 1a) in THF (3.5 mL), butylamine (0.0763 g, 1.04 mmol) was added, and the resulting mixture was stirred at room temperature for 1 hour. The resulting insoluble fraction was collected by filtration and washed by THF (30 mL), and was dried under vacuum. The insoluble part (0.207 g, 0.537 mmol (DTC unit)) was yielded in 62 %.

Reactions with triethylamine, 1,2-diaminoethane and N,N,N-tris(aminomethyl)amine

The reactions were carried out in the same manner as shown for the reaction with butylamine except for varying the respective amounts according to the molar ratios shown in the following Table.

Table. Reaction of the soluble oligomer with amine.

entry	amine	$[DTC]_0 : [NR^aR^bR^c]_0$	gel fraction (%)	appearance
1	NEt_3	1 : 1	**1** was recovered (96 %).	——
2		2 : 1	66	yellow gel
3		1 : 1	62	yellow gel
4		2 : 1	88	yellow powder
5		1 : 1	94	white powder
6		3 : 1	97	yellow powder
7		1 : 1	87	white powder

Synthesis of linear oligomer and polymers

Hydrogen chloride diethyl ether complex (HCl/diethylether, 1M in ether, 0.125 ml, 0.125 mmol) was added to mixture of **1b** (0.732 g, 2.47 mmol) and distilled water (0.0681 g, 3.78 mmol) at room temperature. After the resulting mixture was stirred at room temperature for 24 hours, volatiles were removed under the reduced pressure. The residue was dissolved in tetrahydrofuran (30 ml), and poured into

hexane (400 ml). The mixture of the corresponding linear polymer and oligomer (0.679 g; polymer : M_n = 5680, M_w = 9630, PDI = 1.7; oligomer : M_n = 950, M_w = 1050, PDI = 1.1) was obtained as an yellow oil.

The similar reaction of **1b** (0.644 g, 2.17 mmol) and distilled water (0.0404 g, 2.24 mmol) in the presence of triethylamine (0.0110 g, 0.109 mmol) gave 0.699 g of the mixture of the corresponding linear polymer (M_n = 3520, M_w = 4230, PDI = 1.2) and oligomer (M_n = 820, M_w = 1060, PDI = 1.3).

Spectral data:

^{1}H-NMR ($CDCl_3$, 20 °C) 5.26 (br, -CH_2-C*H*(-O-)-CH_2-), 3.86-3.59 (br), 3.52-3.48 (br), 1.82-1.66 (br, -CH_2-C*H*$_2$-CH_2-), 0.56-0.51 (br, -CH_2-C*H*$_2$-Si-), 0.13-0.10 (br, -Si-C*H*$_3$) ppm.

^{13}C-NMR ($CDCl_3$, 20 °C) 212.3-212.0 (-S-*C*(=S)-O-), 89.9-89.2 (-CH_2-*C*H(-O-)-CH_2-), 74.4-74.3 (-O-*C*H_2-CH_2-), 69.5-69.2 (-CH(-O-)-*C*H_2-OCH_2-), 36.0 (-S-*C*H_2-CH(-O-)-), 23.1-23.0 (-CH_2-*C*H_2-CH_2-), 13.4-12.9(-CH_2-*C*H_2-Si-), –0.26- –0.73 (-Si-*C*H_3) ppm.

^{29}Si-NMR ($CDCl_3$, 20 °C) –19.8, –22.1, –22.8 ppm.

IR (neat) 3471, 2932, 2868, 2803, 1731, 1651, 1477, 1439, 1411, 1345, 1258, 1230, 1188, 1044, 914, 801 cm^{-1}.

It was confirmed that the polymer and oligomers possessed cycDTC moieties by the analyses of NMR spectra. In ^{13}C-NMR spectrum, a signal at around 49 ppm assigned to -O-*C*H_3 was not detected. This indicates that the substitution from -Si-O-CH_3 to -Si-OH and the following condensation were completely produced. The products showed three ^{29}Si-NMR signals at –19.8, –22.1, and –22.8 ppm with the integral ratio of 4 : 3 : 2. On the basis of this information, it is expected that the signals of the cyclic trimer, the cyclic tetramer, and the oligomers having more polymerization degree are observed at around –9, –20, and –22 ppm, respectively. Accordingly, a signal at –19.8 ppm was assigned to the cyclic tetramer. Furthermore, in ^{29}Si-NMR spectrum of the product obtained by the sol-gel reaction in ether, two signals at –19.8 and –22.1 ppm with the integral ratio of

2 : 1 were appeared. In solution reaction, it is expected that the formation of oligomers is prior to the formation of polymers. Signals at –22.1 and –22.8 ppm were reasonably assigned to silicon contained in cyclic or linear oligomers and the chain polymers, respectively.

Synthesis of crosslinked polysiloxanes

Hydrogen chloride diethyl ether complex (HCl/diethylether, 1M in ether, 0.15 ml, 0.15 mmol) was added to mixture of **1a** (0.763 g, 2.44 mmol) and distilled water (0.0700 g, 3.89 mmol) at room temperature. After the resulting mixture was stirred at room temperature for 24 hours, volatiles were removed under the reduced pressure. The residue was washed by $CHCl_3$ (100 ml), to give crosslinked polysiloxane (0.504 g) as an insoluble yellow powder.

The similar reaction of **1a** (0.796 g, 2.55 mmol) and distilled water (0.0600 g, 3.33 mmol) in the presence of triethylamine (0.0100 g, 0.102 mmol) gave the corresponding crosslinked polysiloxane (0.539 g).

Spectral data:
^{13}C-NMR (solid-state (HPDEC), 20 °C) 208.6 (-S-C(=S)-O-), 106.6 (-CH_2-CH(-O-)-CH_2-), 86.4 (-O-CH_2-CH_2-), 69.2 (-CH(-O-)-CH_2-OCH_2-), 46.4 (-Si-OCH_3), 32.1 (-S-CH_2-CH(-O-)-), 19.1 (-CH_2-CH_2-CH_2-), 5.1 (-CH_2-CH_2-Si-) ppm; ^{29}Si (solid-state (HPDEC), 20 °C) –57.4- –67.6 ppm; IR (neat) 3444 (OH), 2937, 2866, 2804, 1731, 1650, 1441, 1345, 1234, 1193, 1099, 1038 cm^{-1}.

A signal at 209 ppm assignable to -C(=S)- was clearly observed in ^{13}C-NMR spectrum. There is no signal around 180 ppm attributable to ring-opened -C(=S)-. ^{29}Si-NMR spectrum is very simple, suggesting the higher conversion of the siloxane group into the polysiloxane structure.

Synthesis of co-polymerization products with trimethoxyvinylsilane

To a mixture of **1a** (1.02 g, 3.26 mmol) and trimethoxyvinylsilane, distilled water (0.168 g, 9.32 mmol) and triethylamine (32.2 mg, 0.318 mmol) was added. By

stirring the mixture at room temperature for 18 h, tetrahydrofurane-insoluble crosslinked polysiloxane (0.860 g) and tetrahydrofurane-soluble oligomers (0.228 g) were obtained. In addition to this example, co-polymerizations in various feed ratios are possible to give the corresponding co-polymers having predictable compositions.

Synthesis of co-polymerization products with glycidoxytrimethoxysilane

To a mixture of **1a** (0.949 g, 3.04 mmol) and glycidoxytrimethoxysilane (0.723 g, 3.06 mmol), distilled water (0.165 g, 9.15 mmol) and triethylamine (30.1 mg, 0.297 mmol) was added. By stirring the mixture at room temperature for 18 h, tetrahydrofuran-insoluble crosslinked polysiloxane (1.13 g) was obtained.

Modification of crosslinked polysiloxane made of 1a

Diethylamine (0.141 g, 1.93 mmol) was added to the crosslinked polysiloxane made of 1a (0.120 g, 0.384 mmol (amount of cycDTC unit)) at room temperature, and the resulting mixture was stirred at room temperature for 10 minutes. The yellow color of the crosslinked polysiloxane disappeared within 10 minutes, indicating the cycDTC was completely consumed to give a product having acyclic thiourethane and thiol groups. After the volatile fractions were removed under the reduced pressure, the residue was washed by $CHCl_3$ (100 ml), and insoluble part of the diethylamine modified product (0.128 g, 0.332 mmol (amount of ring-opened DTC unit), 86 %) was obtained by filtration.

Spectral data:

^{13}C-NMR (solid-state (HPDEC), 20 °C) 188.5-186.4 (-O-C(=S)-N-), 175.4-165.5, 76.6-68.4, 58.7-30.3, 29.5-20.8, 19.6-5.5 ppm.

^{29}Si-NMR (solid-state (HPDEC), 20 °C) –55.2- –71.8 ppm.

IR (KBr) 3445 (OH), 2976, 2933, 2879, 2523 (SH), 1734, 1653, 1559, 1507, 1429, 1362, 1317, 1284, 1245, 1173, 1096, 1063, 1004, 800 cm^{-1}.

In the ^{13}C-NMR spectrum, while a signal at 209 ppm attributed to -C(=S)- in DTC moiety was disappeared, broad signals from 189 to 186 ppm assignable to the ring-opened -C(=S)- were observed. Moreover, ring opening of cycDTC moiety was confirmed by the presence of thiol absorption at 2523 cm^{-1} in the IR spectrum. The ^{29}Si-NMR spectrum was almost same as that of the crosslinked polysiloxane made of **1a**, indicating that the selective reaction of DTC moiety was achieved without damaging siloxane backbone.

Cationic polymerization of cycDTC-Si

To **1a** (0.760 g, 2.43 mmol), methyl trifluoromethanesulfonate (24.9 mg, 0.152 mmol) was added at room temperature, and the mixture was stirred at room temperature. After 2 days, complete consumption of cyclic dithiocarbonate unit was confirmed by NMR-analysis. In the ^{13}C-NMR spectrum, a new signal appeared at 172.5 ppm, attributable to the carbonyl carbon of the acyclic dithiocarbonate, suggesting the formation of the corresponding linear poly(dithiocarbonate). The mixture was dissolved in tetrahydrofuran (5 ml), and the solution was poured into hexane (100 ml) to obtain the corresponding polymer (0.603 g) as precipitates, which were collected by filtration and were dried under vaccum. When the polymer was re-dissolved in tetrahydrofuran, it immediately became insoluble gel by crosslinking, due to moisture-induced sol-gel reaction of the siloxy part in the side chain of the polymer.

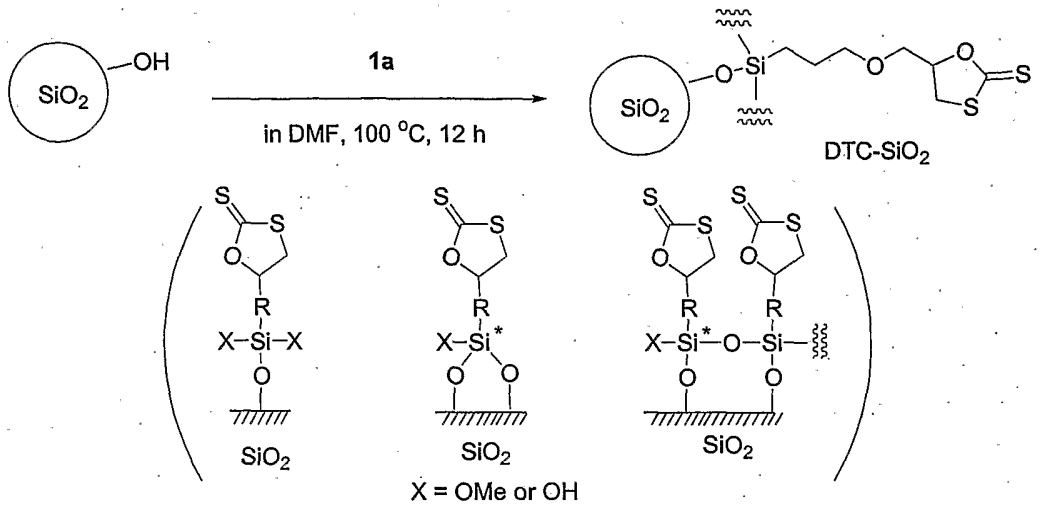
APPLICATION EXAMPLES

Coating of silicate (glass, quartz) surfaces

Coating (pre-treatment) with cycDTC-Si

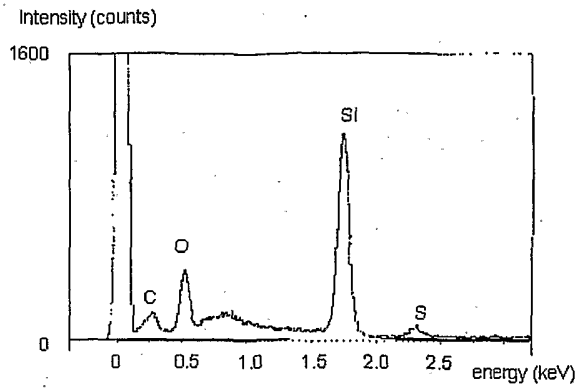
A spherical silica-gel particle, SP-120-40/60 (DAISO Co., Ltd.), whose average diameter was 55 μm, was washed with acetone several times to remove organic impurities, then, dried at 100 °C for 3 hour under reduced pressure. To a silica gel (10.30 g) dispersed in anhydrous dimethylformamide (100 ml), **1a** (10.30 g, 32.96

mmol) was added and the mixture was stirred at 100 °C. After 12 h, the mixture was filtrated through a membrane filter (pore size 0.8 μm), and washed with methanol twice, and further washed with anhydrous tetrahydrofuran in a soxhlet apparatus for 12 hour. The washed silica gel was dried at 60 °C for 5 hours under reduced pressure to obtain 10.33 g of yellowish powder (cycDTC-SiO_2).



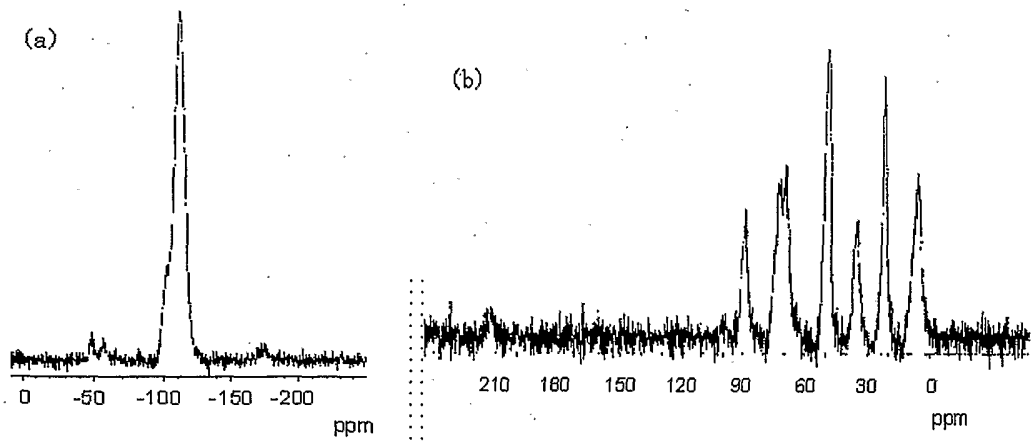
Characterization of the product was performed by SEM, EDX, and elemental analysis.

By the SEM-image of the obtained cycDTC-SiO_2, it was confirmed that the spherical shape of the original silica gel particle was maintained. In the EDX spectrum shown below a signal was observed at 2.30 keV to indicate the presence of sulfur atom on the surface of the silica gel particle. Elemental analysis of the modified silica gel revealed that sulfur content was 3.02 wt-% and consequently the immobilization degree of **1a** on the silica gel surface was calculated to be 0.472 mmol/g.



EDX analysis of cycDTC-SiO_2.

The next figure below shows a solid-state ^{29}Si-NMR spectrum, in which one strong signal due to the silicon atoms of the silica gel was observed around -110 ppm. Two weak signals were also observed around -50 ppm. These weak ones were attributable to the silicon atoms of DTC units bounded to the surface of the silica gel. This NMR analysis suggests that DTC units on the surface of silica gel were covalently bounded by several modes as shown in diagram 5. The presence of the cycDTC moiety on the silica gel was confirmed by a solid state ^{13}C-NMR spectrum, in which there was a signal around 210 ppm attributable to C=S bond:



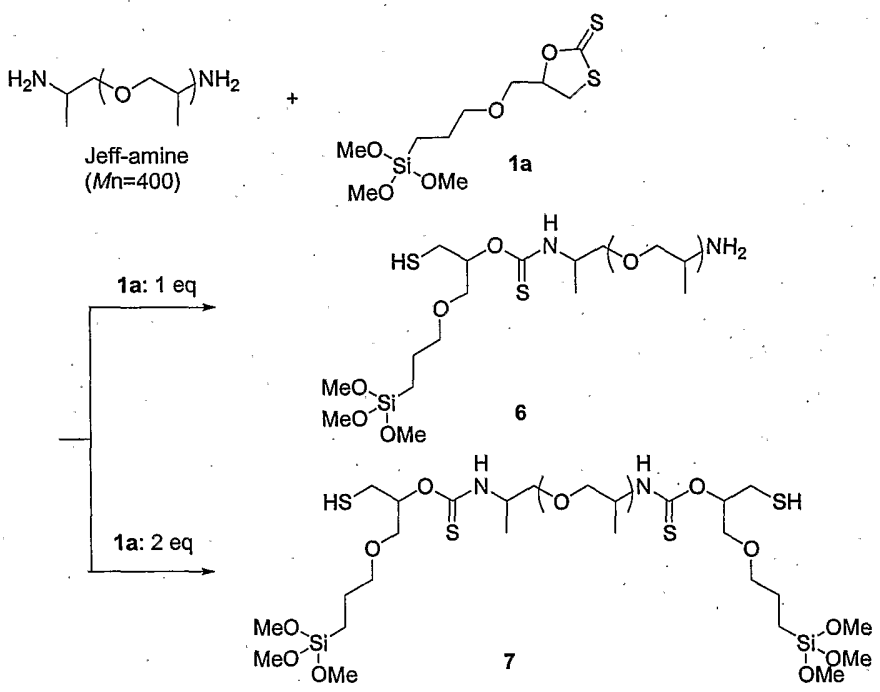
Solid state NMR spectra of cycDTC-SiO_2: (a) ^{29}Si-NMR. (b) ^{13}C-NMR.

Coating with Jeffamine ® modified cycDTC-Si

1st Step: Modification of Jeffamine® with 1a into thiol having siloxy group

Based on the reactivity of **1** with amines, Jeffamine®, a polyether having amino groups at the chain ends was modified into the corresponding polyethers having thiol and siloxy moieties at the chain ends. The procedure is summarized in Scheme 7.

Scheme 7



1a (0.950 g, 3.04 mmol) was added to Jeffamine® (M_n=400; 1.24 g, 3.09 mmol) at room temperature, and the resulting mixture was stirred at room temperature for 1 day. The obtained oil was dissolved in tetrahydrofuran, and precipitated into hexane to obtain the corresponding modified Jeffamine® **6** (1.66 g, M_n = 1060, M_w = 1360, PDI = 1.3) as a viscous yellow oil in a yield of 76%. Similarly, reaction of **1a** (1.95 g, 6.24 mmol) with Jeffamine® (M_n=400; 1.32 g, 3.31 mmol) gave the corresponding modified Jeffamine® **7** (3.04 g, M_n = 1200, M_w = 1400, PDI = 1.2) as a viscous pale yellow oil in a yield of 93%.

6: ^{1}H-NMR($CDCl_3$, 20 °C): 6.41-5.60 (br, -CH_2-C*H*(-O-)-CH_2-), 4.06-3.91 (br), 3.56 (s, -Si-(OC*H*$_3$)$_3$), 3.51-3.28 (br), 3.17-3.07 (br, -N*H*$_2$), 2.90-2.83 (br, -CH(-O-)-C*H*$_2$-SH), 1.70-1.64 (m, -CH_2-C*H*$_2$-CH_2-), 1.20-1.10 (br), 1.01 (d, terminal -O-CH(-C*H*$_3$)-CH_2-), 0.69-0.65 (br, -CH_2-C*H*$_2$-Si-) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 165.5 (-O-*C*(=S)-N-), 76.2-74.8 (br), 73.6-71.6 (br), 67.8, 50.4 (-Si-(O*C*H$_3$)$_3$), 46.8, 46.3, 24.7

(-CH(-O-)-$\underline{C}H_2$-SH), 22.6 (-CH_2-$\underline{C}H_2$-CH_2-), 19.5 (terminal -O-CH(-$\underline{C}H_3$)-CH_2-), 18.4-17.0 (internal -O-CH(-$\underline{C}H_3$)-CH_2-), 5.1 (-CH_2-C$\underline{H_2}$-Si-) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –41.7 ppm; IR (neat) 3333 (NH_2), 2970, 2940, 2870, 1668, 1549, 1455, 1373, 1344, 1298, 1105, 926, 821 cm^{-1}.

7: ^{1}H-NMR ($CDCl_3$, 20 °C): 5.58-5.57 (-CH_2-C$\underline{H}$(-O-)-CH_2-), 4.39 (br), 4.06 (br), 3.78-3.59 (br), , 3.57 (s, -Si-(OC$\underline{H_3}$)$_3$), 3.56-3.38 (br), 3.28-3.25 (br), 3.17-3.11 (br), 2.86 (br), 1.72-1.65 (br, -CH_2-C$\underline{H_2}$-CH_2-), 1.47 (t, -CH_2-S$\underline{H}$,), 1.27-1.25 (br, terminal -O-CH(-$\underline{C}H_3$)-CH_2-), 1.21-1.10 (br, internal -O-CH(-$\underline{C}H_3$)-CH_2-), 0.69-0.63 (br, -CH_2-C$\underline{H_2}$-Si-) ppm; ^{13}C-NMR ($CDCl_3$, 20 °C) 188.2-188.1 (-O-$\underline{C}$(=S)-N-), 79.6, (-CH_2-$\underline{C}$H(-O-)-CH_2-), 78.3, 75.4-74.8 (br), 73.7-72.7 (br), 72.0-7.08 (br), 68.9-68.8 (-CH(-O-)-$\underline{C}H_2$-O), 67.7, 50.3 (-Si-(O$\underline{C}H_3$)$_3$), 25.4, 24.5-24.4 (-CH(-O-)-$\underline{C}H_2$-SH), 22.6-22.5 (-CH_2-$\underline{C}H_2$-CH_2-), 17.6-16.5 (internal -O-CH(-$\underline{C}H_3$)-CH_2-), 5.1-5.0 (-CH_2-C$\underline{H_2}$-Si-) ppm; ^{29}Si-NMR ($CDCl_3$, 20 °C) –41.8 ppm; IR (neat) 3299 (NH), 2969, 2938, 2870, 2841, 2555 (SH), 1677, 1520, 1457, 1374, 1345, 1300, 1258, 1196, 1092, 927, 822 cm^{-1}.

2nd Step: Coating of a glass surface by curing reaction of the modified Jeffamines®

Based on the reactivities of the thiol and siloxy groups of the adducts of **1** with amines (see Scheme 5 and Scheme 6), the modified Jeffamines® **6** and **7** were applied to coating of a glass surface (Scheme 8): The modified Jeffamine® **6** was dissolved in tetrahydrofuran, and was casted on a glass plate. After removal of tetrahydrofuran by slow evaporation in a refrigerator, the glass plate was heated at 50 °C for 24 h. The resulting cured material on the glass plate was insoluble in general organic solvents such as tetrahydrofuran, chloroform, and dimethylformamide, indicating that the condensation reaction of siloxy group resulted in curing reaction of **6**. It can be considered that the formed cured material would be covalently bonded with the glass surface by the reaction of siloxy group with the glass surface. A similar treatment of **7** gave the similar coating material insoluble in tetrahydrofuran, chloroform, and dimethylformamide. In Table 1, thermal properties of the formed coating material are shown. The coating material comprises thiol groups, which can further react with epoxides,

isocyanates, and any other thiol reactive groups for further modification of the coating material.

Scheme 8

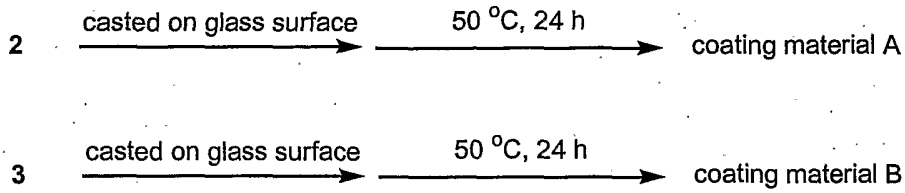


Table 1

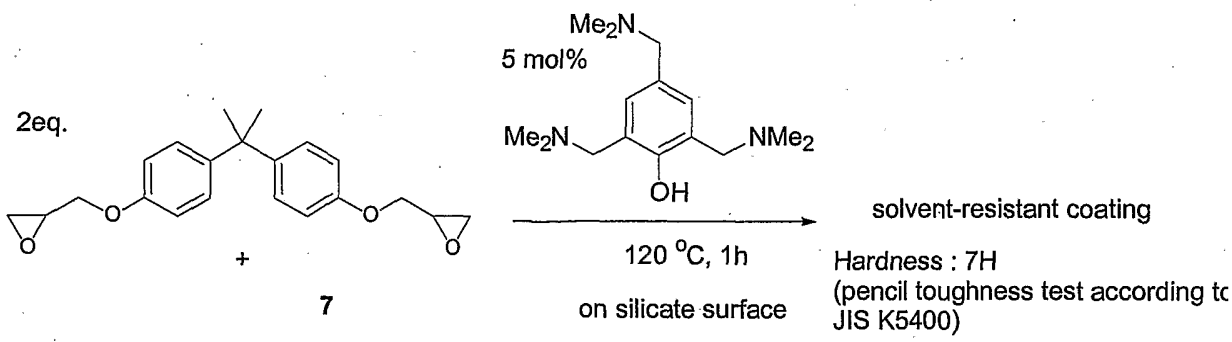
Thermal properties of the cured materials

run	coating	tem. of weight loss (°C)		T_g (°C)
		5%	10%	
1	**A**	174	233	14
2	**B**	207	239	24

Coating with Jeff-amine® modified cycDTC-Si in combination with epoxides

1st Step: Reaction between modified Jeff-amine 7 and epoxide

Scheme 7'



To the modified Jeff-amine 7 (shown in Scheme 7) prepared from Jeff-amine (M_n = 400) (0.574 g, 1.44 mmol) and DTC-Si (0.918 g, 2.94 mmol), it was added: bisphenol A diglycidyl ether (1.023 g, 3.01 mmol) and 2,4,6-tris(dimethylaminomethyl)phenol (0.0320 g, 0.121 mmol). The resulting mixture was stirred at room temperature for 1 hour.

2nd Step: Coating of a glass surface by curing reaction of the epoxy resin product obtained on the 1st Step

The mixture from the 1st step was casted on a glass surface, and cured at 120 °C for 1 hour. The resulting cured resin was insoluble in general organic solvents and water. Mechanical toughness of the layer was tested by pencil toughness test according to the procedure for JIS-K5400, to find that its toughness was graded as 7H.

Coating and bonding of titanium alloys

1st Step: Preparation of sol-gel primers for the application on titanium alloy specimens

Example 1a

1. 500 ml water were placed in a 1000 ml flask and the pH value was adjusted to 7 – 8. Under stirring 46.02 g of 5-(3-trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione (**1a**) were added and the mixture was allowed to swell for 30 minutes.
2. 7.3 ml glacial acetic acid and 10 ml of a 70 % solution (w/v) of zirconium(IV)propylate were diluted with 17 ml of de-ionized water under stirring. Subsequently 300 ml of de-ionized water were added under stirring and the pH value was adjusted to be about 5.
3. The mixture obtained in step 2. was added to the mixture obtained in step 1. under stirring. Subsequently the flask used in step 2. was washed with 200 ml of de-ionized water, which was afterwards added to the

combined mixtures. The resulting mixture was allowed to stand for 30 minutes.

Example 1b

The preparation was performed in the same manner as described for Example 1a, except for replacing 46.02 g 5-(3-trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione by a mixture of 23.0 g 5-(3-trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione and 18.2 g (3-glycidoxypropyl)trimethoxysilane.

Comparative Example 1

The preparation was performed in the same manner as described for Example 1a, except for replacing the 5-(3-trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione (**1a**) by 34 ml (3-glycidoxypropyl)trimethoxysilane.

2nd Step: Pre-treatment of titanium alloy specimens for immersion tests

Cleaning of titanium alloy specimens (Ti6Al4V)

For the experiments titanium tensile shear specimens of the following dimensions 100x25x1.6 mm were used.

First the titanium alloy specimens were submerged in a 500 g/l solution of Turco 5578 in water (an alkaline cleaning agent obtainable from Henkel Surface Technologies Corporation; the above concentration corresponds to approximately 50% (w/v) of an alkali hydroxide) at a temperature of 95 °C for 5 minutes. Next the titanium alloy specimens were rinsed with de-ionized water for 2 minutes.

3rd Step: Applying the sol-gel formulations of Examples 1a, 1b and Comparative Example 1 onto titanium alloy specimens

The titanium alloy sheets were submerged in the sol-gel of Examples 1a, 1b and Comparative Example 1, respectively, for two minutes at room temperature while stirring. Subsequently the excessive sol-gel was allowed to drain for 5 seconds. The specimens were dried for 30 minutes at 60 °C in an air-circulating oven. In addition to the thus primed specimens titanium alloy specimens which were not subjected to sol-gel priming were used as a further control example. Table 2 gives an overview of the different pre-treatment procedures.

Table 2

specimen	pre-treatment procedure
A	only cleaning steps
B	cleaning steps plus pre-treatment with sol-gel of Example 1a
C	cleaning steps plus pre-treatment with sol-gel of Example 1b
D	cleaning steps plus pre-treatment with sol-gel of Comparative Example 1

4th Step: Bonding of pre-treated titanium alloy specimens

To joint the specimens A, B and D the film adhesive Loctite® EA 9696 (Henkel KGaA, Düsseldorf, Germany) was used. Curing of the adhesive was performed at 120 °C for 90 minutes. Those joint specimens were tested in immersion test I.

To joint specimens A, B and C the adhesive Terokal-5070MB-25 – an epoxy resin adhesive based on bisphenol A – (obtainable by Henkel Teroson GmbH, Heidelberg, Germany) was used. Curing of the adhesive was performed at 170 °C for 30 minutes.
Those joint specimens were tested in immersion test II.

Immersion test I –

Determination of aging at 60 °C – Loctite® EA 9696 bonded specimens

To determine aging the joint composites from specimens A, B and D were submerged in de-ionized water at 60 °C and stored for different periods of time, i.e. 0, 720 and 1440 hours, respectively. The results of the immersion test are shown in table 3.

Table 3

specimen	immersion at 60 °C (immersion test I) in hours					
	0		720		1440	
	TSS [MPa]	FP [%cf]	TSS [MPa]	FP [%cf]	TSS [MPa]	FP [%cf]
A	39.5	100	14.6	0	13.6	0
B	>40	100	25.9	90	21.8	80
D	39.3	100	21.9	0	19.0	0

TSS: tensile shear strength
FP: fracture pattern

Specimen A, corresponding to the cleaning pre-treatment only, shows inferior results for tensile shear strength and fracture pattern at 720 and 1440 hours compared to sol-gel pre-treated specimens B and D. The results unambiguously show that the sol-gel, which is prepared using a cyclic dithiocarbonate of the invention (sol-gel B) mediates a significant increase in adhesion properties in the bonding/immersion test. Further the enhanced tensile shear strength and improved fracture pattern clearly shows that sol-gel from Example 1a based on the compounds of the invention acts as superior primer for titanium alloy surfaces even under storage conditions in humid and warm environment.

Immersion test II -

Determination of aging at 70 °C – Terokal-5070MB-25 bonded specimens

To determine aging the joint composites from specimens A, C and D were submerged in de-ionized water at 70 °C and stored for different periods of time, i.e. 0, 21, 42 and 63 days, respectively. The results of the immersion test are shown in table 4.

Table 4

specimen	immersion at 70 °C (immersion test II) in days							
	0		21		42		63	
	TSS [MPa]	FP [%cf]	TSS [MPa]	FP [%cf]	TSS [MPa]	FP [%cf]	TSS [MPa]	FP [%cf]
A	29.6	100	12.5	60	5.7	0	4.3	0
C	31.8	90	18.5	100	18.4	95	17	95
D	23.2	90	18.5	95	17.1	95	14.9	95

TSS: tensile shear strength
FP: fracture pattern
%cf: % cohesive failure

Specimen A (cleaning pre-treatment only), shows inferior long-term characteristics for tensile shear strength and fracture pattern compared to sol-gel pre-treated specimens C and D. The difference between specimens C and D is still remarkable but smaller than in immersion test I. This seems to be due to the use of a combination of both 5-(3-trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione and 18.2 g (3-glycidoxy-propyl)trimethoxysilane in the pre-treatment of specimen C.

Coating and bonding of aluminum alloys

1st Step: Preparation of sol-gel primers for the application on aluminum alloy specimens

Example 2

1. 500 ml water were placed in a 1000 ml flask and the pH value was adjusted to 7 – 8. Under stirring 23.0 g 5-(3-trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione (**1a**) and 18.2 g (3-glycidoxypropyl)trimethoxysilane were added and the mixture was allowed to swell for 30 minutes.
2. 7.3 ml glacial acetic acid and 10 ml of a 70 % solution (w/v) of zirconium(IV)propylate were diluted with 17 ml of de-ionized water under stirring. Subsequently 300 ml of de-ionized water were added under stirring and the pH value was adjusted to be about 5.
3. The mixture obtained in step 2. was added to the mixture obtained in step 1. under stirring. Subsequently the flask used in step 2. was washed with 200 ml of de-ionized water, which was afterwards added to the combined mixtures. The resulting mixture was allowed to stand for 30 minutes.

Comparative Example 2

The preparation was performed in the same manner as described for the Example 2, except for replacing 23.0 g 5-(3-trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione and 18.2 g (3-glycidoxypropyl)trimethoxysilane by 34 ml (3-glycidoxypropyl)trimethoxysilane.

2nd Step: Pre-treatment of aluminum specimens for immersion tests

Cleaning of aluminum specimens (Aluminum 6016 and Aluminum 2024)

In a first step the aluminum specimens were submerged in a 6% solution of Ridoline® 1580 in water (an alkaline degreasing agent obtainable from Henkel KGaA, Düsseldorf, Germany) at a temperature of 60 °C for 5 minutes. In a second step the aluminum specimens were rinsed twice with water for 2 minutes.

Deoxidizing of aluminum specimens

Aluminum 6016 specimens were deoxidized with a 1% solution of Deoxidizer 4902 (deoxidizer on the basis of sulfuric acid and ammonia bifluoride; Henkel KgaA, Düsseldorf, Germany) at room temperature for 2 minutes and subsequently rinsed twice with distilled water.

Aluminum 2024 specimens were deoxidized with a 15 % solution of nitric acid at room temperature by a 5-second-pickling procedure and subsequently rinsed twice with distilled water.

3rd Step: Applying the sol-gel formulations of Example 2 and Comparative Example 2 on aluminum specimens

The cleaned and deoxidized aluminum sheets were submerged in the sol-gel of Example 2 and Comparative Example 2, respectively, for two minutes at room temperature while stirring. Subsequently the excessive sol-gel was allowed to drain for 5 seconds. The specimens were dried for 30 minutes at 60 °C in an air-circulating oven. Table 5 gives an overview of the different pre-treatment procedures.

Table 5

specimen	pre-treatment procedure
E	only cleaning steps
F	cleaning steps plus pre-treatment with sol-gel of Example 2
G	cleaning steps plus pre-treatment with sol-gel of Comparative Example 2

4th Step: Bonding of pre-treated aluminum specimens

To joint specimens A, B and C the adhesive Terokal-5070MB-25 – an epoxy resin adhesive based on bisphenol A – (obtainable by Henkel Teroson GmbH,

Heidelberg, Germany) was used. Curing of the adhesive was performed at 170 °C for 30 minutes.

The joint specimens were tested under the conditions of the above immersion test II.

Immersion test II -

Determination of aging at 70 °C – Terokal-5070MB-25 bonded specimens

To determine aging the joint composites from specimens E, F and G were submerged in de-ionized water at 70 °C and stored for different periods of time, i.e. 0, 21, 42 and 63 days, respectively. The results of the immersion test are shown in table 6.

Table 6

specimen	immersion at 70 °C (immersion test II) in days							
	0		21		42		63	
	TSS [MPa]	FP [%cf]	TSS [MPa]	FP [%cf]	TSS [MPa]	FP [%cf]	TSS [MPa]	FP [%cf]
aluminum 6016								
E	18.3	90	2.7	0	2.1	0	1.1	0
F	18.9	90	16.4	95	14.9	95	13.7	95
G	18.9	90	16.0	90	14.8	95	13.1	95
aluminum 2024								
E	30.4	100	10.2	30	5.1	0	2.2	0
F	31.3	90	19.4	95	16.4	95	15.2	95
G	25.6	90	18.2	95	16.0	95	14.2	95

TSS: tensile shear strength
FP: fracture pattern

Specimen A (cleaning pre-treatment only), shows inferior long-term characteristics for tensile shear strength and fracture pattern compared to sol-gel pre-treated specimens C and D. The difference between specimens C and D is still

remarkable but smaller than in immersion test I. This seems to be due to the use of a combination of both 5-(3-trimethoxysilylpropyloxymethyl)-1,3-oxathiolane-2-thione and 18.2 g (3-glycidoxy-propyl)trimethoxysilane in the pre-treatment of specimen C.

Use of the cyclic dithiocarbonates of the invention as adhesion promoters in adhesives

An aluminum substrate (Al 6016; 100x25x0.8mm) was pre-treated with Alodine 2040, (chrome-free passivation on the basis of hexafluorotitanic acid obatinable from Henkel KgaA, Düsseldorf Germany). The aluminum substrates were bonded together with a base formulation lacking the compounds of the invention and an adhesive formulation containing compound 1a. The curing conditions comprised heating to 120 °C for 60 minutes. Subsequently aging was investigated in a cata-plasma test as described in the following. Bonded composites were wrapped in absorbent cotton which was wetted with de-ionized water. Afterwards the cotton-wrapped composites were further wrapped in aluminum foil and welded into polyethylene foil. The thus-wrapped specimen was stored at 70 °C for 168 and 336 hours, respectively. After aging in humid conditions cold storage at –25 °C for 16 hours was performed. The bonded composites were unwrapped at room temperature and tested for tensile shear strength. The results are summarized in table 7:

Table 7

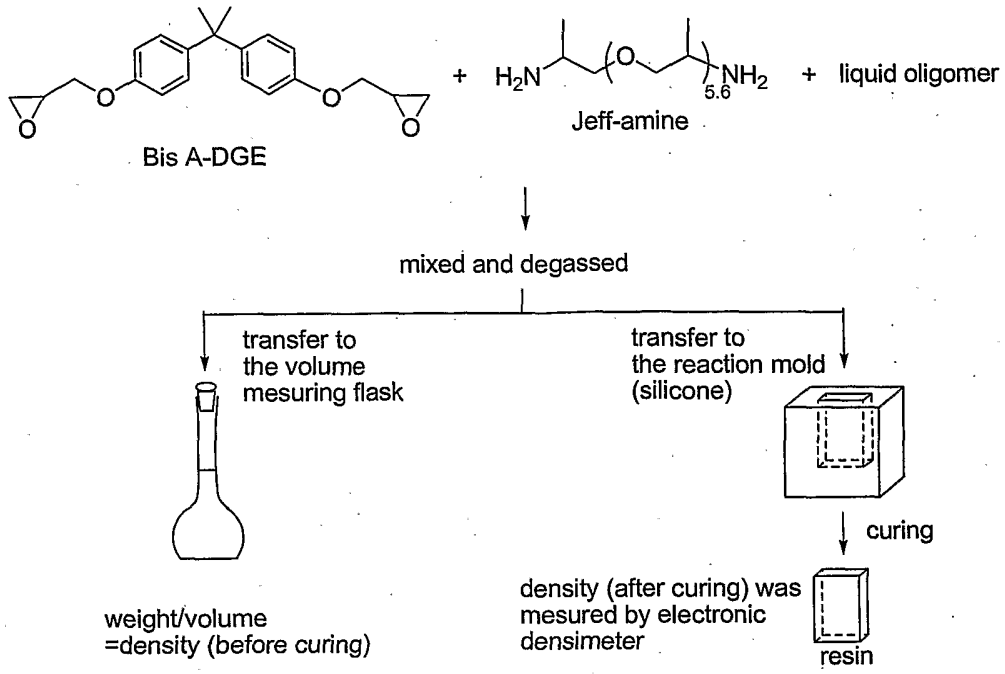
aging under cataplasma conditions in days	tensile shear strength [MPa]	
	base formulation (comparative)	adhesive formulation (according to invention)
0	18.3	16.2
7	9.9	14.4
14	9.6	13.7

base formulation:		adhesive formulation containing compound 1a:	
62,2%	DER 331P (Dow)	60,3%	DER 331P (Dow)
37,8%	Jeffamin D400 (Huntsman)	34,7%	Jeffamin D400 (Huntsman)
		5,0%	compound 1a

DER 331P: epoxy resin based on bisphenol A diglycidyl ether

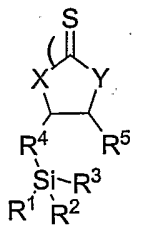
Use of the liquid oligomer as an additive for epoxy-amine curing reaction

Bisphenol A-diglycidylether (0.023 g) and the liquid oligomer (M_n = 560, PDI = 2.06; 0.260 g) described in the preparative section was mixed with stirring under evaculation. To this mixture, Jeff-amine (pre-cooled at 0 °C; 0.786 g) was added and the mixture was mixed with degassing under vaccum below 15 °C for 30 min. The obtained mixture was transferred into a 1 ml volume measuring flask. Based on the weight of 1 ml of the mixture, the density of the epoxy formulation *before* curing was calculated. Then, 1.61 g of the mixture was transferred into a silicone mold (6.0 mm*60mm*70mm), and was cured at 120 °C for 1 h, to obtain 1.59 g of the plate-shaped cured resin. Its density was measured by electronic densimeter. Based on the density values, the degree of volume change was calculated to be -4.4%, according to the equation $(D_{\text{before curing}})/(D_{\text{after curing}})-1$. The volume change observed for the reference experiment in the absence of the liquid oligomer was -6.1%. The following scheme serves to illustrate this experiment:


+ H_2N O NH_2 5.6 + liquid oligomer
Jeff-amine
Bis A-DGE
mixed and degassed
transfer to the volume mesuring flask
transfer to the reaction mold (silicone)
curing
density (after curing) was mesured by electronic densimeter
resin
weight/volume =density (before curing)

CLAIMS

1. A 1,3-oxathiolane-2-thione compound of formula (I):



(I)

wherein

R^1 and R^2 are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue,

R^3 is different or the same as R^1 or R^2 or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, or an araliphatic or heteroaraliphatic residue,

R^4 is a bridging group selected from the groups consisting of aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic and heteroaromatic groups and

R^5 is hydrogen, an aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic, heteroaromatic, cycloaliphatic or heterocycloaliphatic group or

R^4 and R^5 form a cycloaliphatic, cycloheteroaliphatic, aromatic or heteroaromatic residue, which is optionally substituted with an aliphatic, heteroaliphatic residue serving as a bridging group to the silicone atom and

X and Y are different and selected from oxygen and sulfur and

mixtures of such compounds.

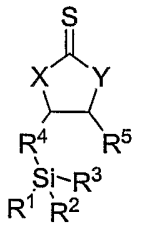
2. The 1,3-oxathiolane-2-thione compound according to claim1,
wherein R^1, R^2 and R^3 are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 4 carbon atoms.

3. The 1,3-oxathiolane-2-thione compound according to claim 1 or 2,

wherein R^1, R^2 and R^3 are the same or different, each of which denotes a methoxy or ethoxy residue.

4. The 1,3-oxathiolane-2-thione compound according to any of claims 1 to 3 wherein
R^4 is $-(CH_2)_3OCH_2-$ and R_5 is hydrogen or
R^4 and R^5 together form $-(CH_2-CH_2-CHR^X-CH_2)-$ whereby R^X is $-CH_2-CH_2-$.

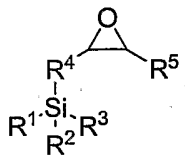
5. A method for the preparation of compounds having the general of formula (I):



(I)

wherein
R^1 and R^2 are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue,
R^3 is different or the same as R^1 or R^2 or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, or an araliphatic or heteroaraliphatic residue,
R^4 is a bridging group selected from the groups consisting of aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic and heteroaromatic groups and
R^5 is hydrogen, an aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic, heteroaromatic, cycloaliphatic or heterocycloaliphatic group or
R_4 and R_5 form a cycloaliphatic, cycloheteroaliphatic, aromatic or heteroaromatic residue, which is optionally substituted with an aliphatic, heteroaliphatic residue serving as a bridging group to the silicone atom and
X and Y are different and selected from oxygen and sulfur, characterized in that

an epoxy compound of general formula (II):



(II)

wherein R^1, R^2, R^3, R^4 and R^5 are the same as in formula (I), is brought to reaction with carbon disulfide in the presence of a catalyst.

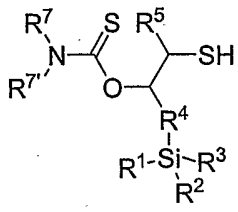
6. The method according to claim 5, wherein the catalyst is at least one alkali metal halide, selected from the group consisting of "lithium chloride, lithium bromide, lithium iodide, sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, potassium iodide".

7. The method according to claim 5 or 6, wherein the catalyst is lithium bromide.

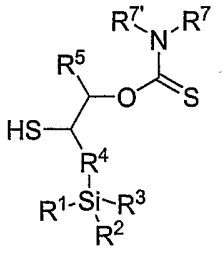
8. The method according to any of claims 5, 6 and 7, whereby the reaction is performed in the presence of an organic solvent or mixture of organic solvents.

9. The method according to claim 8, whereby the organic solvent is a linear or cyclic ether, amide, alcohol, nitrile, ketone or a mixture thereof.

10. A compound of general formula (IIIa) or (IIIb):



(IIIa)



(IIIb)

wherein

R^1 and R^2 are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue,

R^3 is different or the same as R^1 or R^2 or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, or an araliphatic or heteroaraliphatic residue,

R^4 is a bridging group selected from the groups consisting of aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic and heteroaromatic groups and

R^5 is hydrogen, an aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic, heteroaromatic, cycloaliphatic or heterocycloaliphatic group or

R^4 and R^5 form a cycloaliphatic, cycloheteroaliphatic, aromatic or heteroaromatic residue, which is optionally substituted with an aliphatic, heteroaliphatic residue serving as a bridging group to the silicone atom,

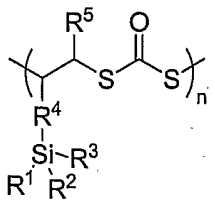
whereby (IIIa) and (IIIb) are

obtainable by reaction of a compound according to one of claims 1 to 4 with an amine having the general formula $HNR^7R^{7'}$ or a polymeric polyamine,

wherein R^7 and $R^{7'}$ are the same or different and denote hydrogen, a straight-chain or branched aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic or heteroaromatic group.

11. The compound according to claim 10 wherein the polymeric polyamine is a polyoxyalkylene diamine or polyoxyalkylene triamine with a number-average molecular weight of 200 to 5000, preferably 200 to 1000.

12. A polymeric compound of general formula (IV):



(IV)

wherein

R^1 and R^2 are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue,

R^3 is different or the same as R^1 or R^2 or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, or an araliphatic or heteroaraliphatic residue,

R^4 is a bridging group selected from the groups consisting of aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic and heteroaromatic groups and

R^5 is hydrogen, an aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic, heteroaromatic, cycloaliphatic or heterocycloaliphatic group or

R^4 and R^5 form a cycloaliphatic, cycloheteroaliphatic, aromatic or heteroaromatic residue, which is optionally substituted with an aliphatic, heteroaliphatic residue serving as a bridging group to the silicone atom,

and n is from 2 to 1000,

obtainable by cationic polymerization of one or more compounds according to claims 1 to 4.

13. A liquid or solid sol-gel product obtainable by acid or base catalyzed reaction of one or more compounds according to claims 1 to 4, 10, 11 or 12 in the presence or absence of further silyl compounds of the general formula $SiR^{1'}R^{2'}R^{3'}R^6$ wherein

$R^{1'}$ and $R^{2'}$ are the same or different, each of which denotes a straight-chain or branched alkoxy residue with 1 to 6 carbon atoms or an aryloxy or aralkyloxy residue,

$R^{3'}$ is different or the same as R^1 or R^2 or an aliphatic residue, an amino residue, a halogen residue, an aromatic or heteroaromatic residue, or an araliphatic or heteroaraliphatic residue and

R^6 denotes a straight-chain or branched aliphatic, heteroaliphatic, araliphatic, heteroaraliphatic, aromatic or heteroaromatic group.

14. A solid sol-gel product obtainable by reaction of the liquid sol-gel product of claim 13 with amines and/or epoxy compounds.

15. A disulfide group containing compound or sol-gel product formed by reaction of a compound according to any of claims 10 or 11 or a sol-gel product according to claims 13 or 14 by oxidative coupling of thiol groups.

16. Use of the liquid sol-gel products of claims 13, 14 or 15 in surface coating, surface pre-treatment and material bonding.

17. The use according to claim 16 wherein the surface or material is glass, silicone, a pure metal or an alloy.

18. The use according to claim 17 wherein the metal is and/or the alloy contains one or more of the following metals "aluminum, titanium, copper, steel, gold and silver".

19. The use according to any of claims 16 to 18 wherein the surface is a macroscopically flat surface or the surface of small particles.

20. The use according to any of claims 16 to 19 wherein the liquid sol-gel product is subsequently cured to produce particles coated by crosslinked sol-gels, macroscopically flat surfaces coated by crosslinked sol-gels or bonded composites comprising crosslinked sol-gels between the bonded materials.

21. The use according to claim 20 wherein the coated particles are stationary phase particles for column chromatography or scavenger particles for binding of amines.

22. The use according to claim 20 wherein the coated macroscopically flat surfaces are silicon wafer surfaces.

23. Use of a polymeric material according to claim 12 as an optical material.

24. Use of any of the 1,3-oxathiolane-2-thione compounds of claims 1 to 4, thiourethane compounds of claims 10 and 11 or polymeric compounds of claim 12 or any liquid sol-gel product of claims 13 or 15 in adhesive formulations.

25. The use of claim 24 wherein compounds or sol-gel products are present in a concentration of up to 20 wt.-%, preferably 0.1 to 10 wt.-% and most preferably 1 to 5 wt.-%.

26. The compound of claim 10, wherein the thiol group is further reacted with a compound selected from the group consisting of "epoxides, isocyanates, isothiocyanates, thiols and carboxylic acid derivatives".

27. The compound of claim 11, being further reacted with an epoxy compound, preferably a bisphenol A diglycidyl ether.

28. A solid sol-gel product obtainable by reaction of the liquid sol-gel product of claim 13 by applying heat.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/003602

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G77/28 C08G75/28 C08G75/14 C07F7/18

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 7 C08G C07F C07D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	abstract	1-28
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 14, 22 December 1999 (1999-12-22) -& JP 11 246632 A (KYOWA YUKA KK), 14 September 1999 (1999-09-14) cited in the application	1-4, 12-14, 16-23
Y	abstract	1-28
Y	US 3 278 484 A (TESORO GIULIANA C) 11 October 1966 (1966-10-11) claim 1	1-28

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

[X] Patent family members are listed in annex.

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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 August 2004	13/08/2004

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

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

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International Application No
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