

SPECIFICATION

Preparation of Bis-(silylethyl)-oligosulphides

This invention relates to a process for the preparation of bis-(silylethyl)-oligosulphides and to such compounds when prepared by this process.

It is known that bis-(alkoxysilylalkyl)-oligosulphides may be prepared from the corresponding alkoxy silyl alkyl mercaptans by direct reaction with sulphur (German Patent No. 2,405,758). The same oligosulphidic silanes may be obtained even more simply and conveniently from the alkoxy silyl alkyl halides by a single reaction with, in particular, alkali metal hydrogen sulphides and sulphur. In this case, excess hydrogen sulphide is formed (German Offenlegungsschrift No. 2,542,534).

It is also known that bis-(alkoxysilylalkyl)oligosulphides may be prepared from the corresponding disulphides by reaction with sulphur at temperatures of from 100 to 200°C (German Offenlegungsschrift No. 2,360,471).

The above-mentioned oligosulphides contain at most 6 sulphur atoms forming as it were a bridge between the two alkyl groups attached to the silicon, the alkyl groups containing from 1 to 10 carbon atoms.

Furthermore, it is known that silyl alkyl thioethers may be obtained from vinyl silanes by reaction with hydrogen sulphide (German Auslegeschrift No. 1,000,817).

Oligosulphidic silanes have acquired considerable significance as additives in rubber mixtures containing silica filler, *inter alia*, for improving the mechanical properties of the vulcanisates (German Patent No. 2,255,577).

It is also possible to introduce sulphur-free silanes containing unsaturated organic groups as ligand on the silicon atom into mixtures based on certain rubbers. It is also known that silyl alkyl thioethers do not produce advantageous rubber properties in vulcanisates and that, among other disadvantages, mercapto-silanes give off an intense, very unpleasant odour.

An object of the present invention is to provide a process for the preparation of sulphur-containing silanes which may be easily and effectively incorporated, for example, into rubber mixtures containing silicate fillers and which, *inter alia*, impart particularly favourable properties to the vulcanisates obtained therefrom.

It has now been found that bis-(silylethyl)-oligosulphides containing up to more than 7 sulphur atoms in the molecule may be prepared by the present process.

It has been found that the products obtained by the process according to the present invention are not identical with the known, above-mentioned oligosulphidic silanes (German Offenlegungsschrift No. 2,542,534). Compared with the additives according to the above-mentioned German Patent No. 2,255,577, the silanes prepared by the process according to the present invention enable substantially the same outstanding and, in some cases, even better results to be obtained in rubber mixtures and the vulcanisates thereof.

In general terms, the present process effects the addition of sulphur with organosilanes containing ethylenically unsaturated organic groups and is preferably carried out under autogenous pressure and at elevated temperature. During the reaction, which may even be carried out in the presence of hydrogen sulphide, the elemental sulphur is apparently incorporated into the organosilane molecule in such a way that sulphur bridges containing more than one sulphur atom in the molecule, depending on the quantity of sulphur used, are formed.

The present invention provides a process for the preparation of a bis-(silylethyl)-oligosulphide corresponding to the following average formula (I):



wherein

R represents chlorine, bromine, iodine, C₁—C₃ alkoxy, 2-methoxy ethoxy, 2-ethoxy ethoxy or hydroxy;

R¹ represents C₁—C₃ alkyl, phenyl or C₅—C₇ cycloalkyl;

n represents 0, 1 or 2;

m represents 1 or 2; such that m+n represents 1, 2 or 3; and

x represents a number of from 2.0 to 8.0.

which comprises reacting a vinyl silane corresponding to the following formula (II):



wherein R, R¹, n and m are as defined in above; with sulphur and, optionally, hydrogen sulphide, in a molar ratio of vinyl silane:sulphur of from 1:2.5 to 1:10 and a molar ratio of vinyl silane:hydrogen sulphide of from 1:0 to 1:5, at a temperature from 100 to 200°C, under a pressure of from 1 to 25 bars and in the presence of a sulphidation catalyst.

It is assumed that, particularly where relatively large quantities of sulphur are used, some of the sulphur is incorporated in the form of chain-branching of the sulphur bridge between the silyl alkyl

groups. Even if hydrogen sulphide is not additionally used, sulphur-containing compounds and compound mixtures are evidently formed and, by comparison with known oligosulphidic silanes, produce equally good and, in some cases, even better processing properties of rubber moulding compositions and also rubber properties of vulcanisates produced therefrom, the reactions both with and without hydrogen sulphide being carried out under pressure and at a temperature which is generally above the boiling point of the corresponding silane starting materials.

It is possible by the process according to the present invention to produce silanes containing up to 8 sulphur atoms in the molecule, even if only one unsaturated organic group is available per silane starting molecule. However, it has been found that the quantity of sulphur used may reach an optimum in terms of practical application. In general, this optimum quantity amounts to approximately 7.5 moles of elemental sulphur per mole of silane used and is governed to some extent by the particular silane reacted. A quantity of sulphur distinctly in excess of this optimum quantity does not afford significant advantages in terms of rubber technology, but only makes the reaction mixtures difficult to work-up because the unreacted sulphur or the sulphur which separates after cooling of the reaction products has to be removed, for example by filtration.

Of the total sulphur content of the synthesised compounds, the analytically determinable polysulphidically-bound sulphur is particularly effective in terms of practical application, particularly in rubber technology.

NMR-spectra were recorded from the silanes produced in accordance with the present invention. The evaluation thereof suggests that, in consequence of the reaction without hydrogen sulphide, the arrangement of the sulphur atoms in the silanes is far less defined and established than where the alternative reaction is adopted, in respect of which it is assumed that the addition of hydrogen sulphide with the double bond of the unsaturated compounds with initial formation of the corresponding mercaptan takes place in a first stage and the following addition of the mercaptan initially formed with a double bond of another molecule with simultaneous incorporation of elemental sulphur into the chain takes place in a second stage.

It has been found that, even at greatly increased temperature and pressure, the above-mentioned reactions do not take place to a significant extent or at a sufficient velocity or in such a favourable direction in terms of rubber technology if they are carried out in the absence of a catalyst. It has been found that basic substances, such as alkalis, amines, quaternary ammonium compounds and, above all, sodium ethylate, potassium ethylate, sodium methylate and sodium isopropylate, for example, are particularly suitable catalysts. Even where hydroquinones are used as catalysts, equally good results are obtained, particularly where hydroquinone itself is used.

The temperature may be varied within relatively wide limits of from 100 to 210°C without adversely affecting the quality of the reaction products and, as usual, is related to the reaction time. A combination of a reaction temperature of 150°C and a reaction time of 7 hours has proved to be particularly advantageous. Below a temperature of about 100°C, the reaction gives a product having no value in terms of rubber technology. At reaction temperatures distinctly above 200°C, for example at about 250°C, the reaction products begin to decompose.

The reaction pressure, i.e. the total pressure prevailing at the particular reaction temperature, may also vary within wide limits, i.e. from 1 to 25 bars. It may be adjusted, for example by the introduction of hydrogen sulphide under pressure. In general, the autogenous pressure is sufficient.

The molar ratio of silane:sulphur is selected according to the required amount of sulphur in the molecule of the silane according to the present invention and amounts to from 1:2.5 to 1:10.

Where hydrogen sulphide is additionally used, the molar ratio of vinyl silane:hydrogen sulphide may amount to from 1:0.1 (1:0 signifies the absence of H₂S) to 1:5.

During the reaction, it is particularly important to ensure, by using suitable apparatus, that the elemental sulphur which is liquid at the elevated reaction temperature is more effectively reacted with the silane by intensive mixing. On completion of the reaction, the reaction mixture is left to cool with continued stirring and further processed as described below.

The following are examples of suitable vinyl silane reactants: vinyl trichlorosilane, vinyl methyl dichlorosilane, vinyl phenyl dichlorosilane, vinyl diphenyl chlorosilane, vinyl dimethyl chlorosilane, vinyl trimethoxy silane, vinyl triethoxy silane, vinyl tripropoxy silane, vinyl-tris-*i*-propoxy silane, vinyl-tris-(2-methoxyethoxy)-silane, divinyl dichlorosilane, divinyl dibromosilane and diiodosilane, divinyl diethoxy silane, divinyl dimethoxy silane, divinyl di-*i*-propoxy silane, divinyl-di-*n*-propoxy silane, vinyl methyl dimethoxy silane, vinyl ethyl diethoxy silane, vinyl methyl-di-(2-ethoxy-ethoxy)-silane, vinyl diethyl ethoxy silane, vinyl dimethyl methoxy silane, vinyl diethyl-2-methoxy ethoxy silane, vinyl phenyl diethoxy silane, vinyl diphenyl methoxy silane, vinyl cyclohexyl diethoxy silane, vinyl cyclopentyl diethoxy silane and vinyl cycloheptyl dimethoxy silane. It is preferred to use monovinyl silanes.

The optional hydrolysis or partial hydrolysis of the reaction products obtained in accordance with the present invention may be carried out by known methods, hydrolysable groups R being converted into hydroxy groups.

(Referring to the accompanying drawings, all of the reproduced 60 MHz H¹ NMR-spectra were recorded under the following conditions: solvent CDCl₃; temperature 37°C; filter band width 4 Hz; R.F.

field 0.02 mG; recording time 250 s; recording range 500 Hz; spectrum amplitude 8. The internal standard was tetramethyl silane ($\delta=0$). The NMR-spectra include the integration curves).

Example 1

In a 1.5-litre capacity stirrer-equipped vessel, 300 g of sulphur in powder form (corresponding to 9.37 moles) are dispersed in 238 g of vinyl triethoxy silane (1.25 moles) by means of a blade stirrer. The resulting dispersion is introduced into a 2-litre capacity pressure vessel equipped with an automatic stirrer. Following the addition of 12 g of hydroquinone as catalyst, the pressure vessel is closed and its contents heated to 150°C over a period of 30 minutes during which the pressure rises to about 5 bars. The reaction is continued under these conditions for 7 hours with intensive stirring. The reaction mixture is then cooled and the pressure released. The unreacted sulphur is filtered off. The residual reaction product is a pale reddish-brown, clear slightly oily liquid which has a total sulphur content of 39.1%, by weight, and a polysulphur content of 24.9%, by weight. Unsaturated carbon atoms emanating from the vinyl groups may no longer be detected.

Practical testing of the reaction product in a styrene/butadiene rubber test mixture containing silica filler both in the case of conventional cross-linking with sulphur and also in the case of elemental sulphur-free cross-linking with the sulphur-containing reaction product revealed a considerable increase in tensile strength by comparison with a conventional oligosulphidic silane, coupled with equally good or improved moduli and distinctly increased cross-linking kinetics.

Example 2

The procedure was as in Example 1, except that, before heating, hydrogen sulphide was introduced into the autoclave to a pressure of 10 bars. The reaction time and temperature were the same. The total sulphur content of the filtered clear reaction product now amounted to 27.6%, by weight, and the content of polysulphidic sulphur to 17.6%, by weight. The NMR-spectrum of the reaction product is shown in Figure 1 of the accompanying drawings.

Practical rubber testing in accordance with Example 1 showed that, again by comparison with a conventional oligosulphidic silane, the reaction product prepared with the additional use of H_2S brings about a distinct increase in the cross-linking kinetics both where vulcanisation is carried out with sulphur and where cross-linking is carried out in the absence of elemental sulphur. At the same time, the tensile strength (DIN 53 504) of the vulcanisate or cross-linked product is distinctly increased, while the measured values for the moduli, shock elasticity (ASTM D 624) and tear propagation resistance (DIN 53 507) reach or almost reach the already very good values of the comparison silane.

Example 3

If the procedure of Example 1 is repeated under the same conditions, but using vinyl silane and sulphur in a molar ratio of 1:10, a reaction product is obtained which contains 33.4%, by weight, of total sulphur and 18.8%, by weight, of polysulphidic sulphur, the NMR-spectrum of which is shown in Figure 2 of the accompanying drawings. The practical rubber testing of this reaction product again shows improved test values by comparison with the known oligosulphidic silane. The increase in the cross-linking kinetics and a reduction in the incubation time by the reaction product both with sulphur-containing and with sulphur-free cross-linking of the shaped rubber compositions are again remarkable.

Example 4

If the procedure of Example 3 is repeated with only the reaction time being increased (to 21 hours), a reaction product is obtained which has an increased content of polysulphidic sulphur (20.1% by weight), but a lower total sulphur content (30.7%, by weight). The NMR-spectrum of this product is shown in Figure 3 of the accompanying drawings.

Testing of the reaction product in rubber moulding compositions and vulcanisates again shows good results, such as, in particular, an increase in the cross-linking velocity and an increase in the tensile strengths after vulcanisation (sulphur-free and sulphur-containing) and, for example, an increase in tear propagation resistance (DIN 53 507) after sulphur-free cross-linking.

Example 5

A reaction product is again prepared under the same conditions and using the same quantities as in Examples 1 and 3, but using a ratio of vinyl triethoxy silane to sulphur of 1:5. It has a total sulphur content of 36.6%, by weight, and a polysulphidic sulphur content of 22.9%, by weight. The NMR-spectrum of this reaction product is shown in Figure 4 of the accompanying drawings. The high sulphur content of both types gives particularly advantageous results in practical rubber testing; a distinctly increased cross-linking velocity by comparison with the results obtained with the known oligosulphidic silane "S 69"; also a more favourable cross-linking conversion, particularly where vulcanisation is carried out with sulphur, a distinctly improved tensile strength (DIN 53 504), at least equally good moduli and tear propagation resistance (DIN 53 507) and slight increases in Shore A hardness.

Example 6

Following the procedure of Example 2, a reaction product was produced adopting the following modifications, hydrogen sulphide being additionally used, H_2S pressure 11 bars, reaction temperature 200°C (reaction time: 7 hours), vinyl triethoxy silane and sulphur in a molar ratio of 1:10. The reaction product had a total sulphur content of 25.2 and a polysulphide sulphur content of 14.5%, by weight. The NMR-spectrum thereof is shown in Figure 5 of the accompanying drawings.

The practical rubber testing of this reaction product shows that the measured values are at the same level as the corresponding values of Example 2, being more favourable in some instances (cross-linking kinetics, tear propagation resistance) and less favourable in others (tensile strength, moduli),

10	Example	1	2	3	4	5	6	10
	Total sulphur content ⁽¹⁾	39.1	27.6	33.4	30.7	36.6	25.2	
	x (calculated) ⁽²⁾	7.6 ⁽³⁾	4.5	6.0	5.2	6.9	4.0	
	(1)							
	(2) as determined by analysis in % sulphur content of —S _x —							
15	(3) probably a mixture of compounds with, for example, —S ₇ — and —S ₈ —							15

The following rubber mixtures and the vulcanisates or crosslinked products produced therefrom were tested to assess the usefulness of the silanes according to the present invention (cf. Example 4) and to demonstrate the superior effect thereof.

		<i>Mixture No. (quantities in parts, by weight)</i>							
20	Constituents	V1	E1.1	E2.1	E3.1	E4.1	E5.1	E6.1	20
	Styrene-butadiene rubber (SBR 1500)	100	100	100	100	100	100	100	
	Silica filler ⁽¹⁾	40	40	40	40	40	40	40	
	Zinc oxide (red seal quality)	3	3	3	3	3	3	3	
	Stearic acid	2	2	2	2	2	2	2	
25	Silane "Si 69" ⁽²⁾	3	—	—	—	—	—	—	25
	Silane according to Example 1	—	3	—	—	—	—	—	
	Silane according to Example 2	—	—	3	—	—	—	—	
	Silane according to Example 3	—	—	—	3	—	—	—	
	Silane according to Example 4	—	—	—	—	3	—	—	
30	Silane according to Example 5	—	—	—	—	—	3	—	30
	Silane according to Example 6	—	—	—	—	—	—	3	
	N,N-dimethyl-N,N-diphenyl thiuram disulphide	—	—	—	—	—	—	—	
	Benzothiazyl-2-cyclohexyl								
35	sulphenamide	1	1	1	1	1	1	1	35
	Sulphur	2	2	2	2	2	2	2	

⁽¹⁾ Prepared by precipitation; active; specific surface (DIN 66 132) 175 m²/g; mean primary particle size 18 μm

⁽²⁾ bis-(3-triethoxysilylpropyl)-oligosulphide having a minimum sulphur content of 22.0%, by weight, according to the prior art.

		<i>Mixture No. (quantities in parts, by weight)</i>							
40	Constituents	V2	E1.2	E2.2	E3.2	E4.2	E5.2	E6.2	40
	Styrene-butadiene rubber (SBR 1500)	100	100	100	100	100	100	100	
	Silica filler ⁽¹⁾	40	40	40	40	40	40	40	
45	Zinc oxide (red seal quality)	3	3	3	3	3	3	3	45
	Stearic acid	2	2	2	2	2	2	2	
	Silane "Si 69" ⁽²⁾	3	—	—	—	—	—	—	
	Silane according to Example 1	—	3	—	—	—	—	—	
	Silane according to Example 2	—	—	3	—	—	—	—	
50	Silane according to Example 3	—	—	—	3	—	—	—	50
	Silane according to Example 4	—	—	—	—	3	—	—	
	Silane according to Example 5	—	—	—	—	—	3	—	
	Silane according to Example 6	—	—	—	—	—	—	3	
	N,N-dimethyl-N,N-diphenyl thiuram disulphide								
55	disulphide	2	2	2	2	2	2	2	55
	Benzothiazyl-2-cyclohexyl								
	sulphenamide	—	—	—	—	—	—	—	
	Sulphur	—	—	—	—	—	—	—	

⁽¹⁾ prepared by precipitation; active; specific surface (DIN 66 132) 175 m²/g; mean primary particle size 18 μm

⁽²⁾ bis-(3-triethoxysilylpropyl)-oligosulphide having a minimum sulphur content of 22.0%, by weight, according to the prior art.

The first half of the rubber mixtures comprising the comparison mixture V1 according to the prior art and the mixtures according to the present invention (use of the present silanes in rubber compositions) E1.1 to E6.1 containing the present silanes of Examples 1 to 6 was conventionally vulcanised with sulphur and accelerators. The second half of the rubber mixtures comprising the comparison mixture V2 according to more recent prior art (cf., for example, German Patent No. 2,536,674; British Patent No. 1,524,077 or French Patent No. 75 26 918) and the mixtures according to the present invention E1.2 and E6.2 also containing the present silanes according to Examples 1 to 6 was cross-linked with the oligosulphidic silanes in the presence of accelerators, but in the absence of elemental sulphur.

The rubber mixtures were tested (for example for the cross-linking kinetics) in accordance with DIN 53 529 (Preliminary Standard of October 1972) entitled "Vulvametry" (also known as the Rheometer Test): deformation amplitude 3°; test frequency 3 cycles per minute; test temperature 155°C; Monsanto MPV Rheometer. $t_{10\%}$ is the reaction time (vulcanisation time) up to 10% conversion in minutes and $t_{90\%}$ is the reaction time up to a 90% conversion. The difference between $t_{90\%}$ and $t_{10\%}$ is a measure of the reaction kinetics, shorter times being indicative of greater kinetics.

The tensile strengths and moduli (both measured in kp/cm^2) of the corresponding vulcanisates and cross-linked products (vulcanisation and crosslinking temperature 155°C) were measured in accordance with DIN 53 504 and the tear propagation resistances and Shore-A hardnesses thereof in accordance with DIN 53 507 and DIN 53 505, respectively.

The results are set out in the following Table.

The evaluation of the results may be found above after the corresponding Example.

Results

Tests and determinations	Mixtures or the vulcanisates thereof						
	V1	E1.1	E2.1	E3.1	E4.1	E5.1	E6.1
$t_{90\%}-t_{10\%}$	28.8	81.1	22.4	21.1	22.3	22.6	21.6
Tensile strength	14.4	18.2	18.5	15.5	18.6	18.3	17.4
Modulus 300%	59	63	54	58	57	59	57
Tear propagation resistance	16	14	19	16	17	16	20
Shore Hardness	64	67	64	67	64	66	64

Tests and determinations	Mixtures or the vulcanisates thereof						
	V2	E1.2	E2.2	E3.2	E4.2	E5.2	E6.2
$t_{90\%}-t_{10\%}$	8.8	3.6	5.5	4.0	4.5	3.8	4.8
Tensile strength	18.7	20.3	23.0	28.8	19.6	17.4	22.8
Modulus 300%	59	57	55	58	53	63	47
Tear propagation resistance	16	17	19	22	23	18	24
Shore hardness	65	67	66	65	65	67	64

Claims

1. A process for the production of a bis-(silylethyl)-oligosulphide corresponding to the following average formula (I)



wherein

R represents chlorine, bromine, iodine, C_1-C_3 alkoxy, 2-methoxy ethoxy, 2-ethoxy ethoxy or hydroxy;

R' represents C_1-C_3 alkyl, phenyl or C_5-C_7 cycloalkyl;

n represents 0, 1 or 2;

m represents 1 or 2; such that $m+n$ represents 1, 2 or 3; and

x represents a number of from 2.0 to 8.0, which comprises reacting a vinyl silane corresponding to the following formula (II):



wherein

R, R' , n and m are as defined in claim 1; with sulphur and, optionally, hydrogen sulphide, in a molar ratio of vinyl silane:sulphur of from 1:2.5 to 1:10 and a molar ratio of vinyl silane:hydrogen sulphide of from 1:0 to 1:5, at a temperature of from 100 to 200°C, under a pressure of from 1 to 25 bars and in the presence of a sulphidation catalyst.

2. A process as defined in claim 1, wherein R represents C_1-C_3 alkoxy or chlorine; n represents 0; m represents 1; and x represents a number from 2.0 to 8.0.

3. A process as claimed in claim 1 or 2 in which the reaction product is at least partially hydrolysed.

4. A process for the preparation of a bis-(silylethyl)-oligosulphide substantially as described with particular reference to any of the Examples.
5. A bis-(silylethyl)-oligosulphide of formula (I) as defined in claim 1 or 2, when prepared by a process as claimed in any of claims 1 to 4.
- 5 6. A silicate filler-containing, cross-linkable rubber composition which contains a bis-(silylethyl)-oligosulphide as claimed in claim 5.
7. A process for the production of a silicate filler-containing, cross-linkable rubber composition which comprises incorporating into such a composition a bis-(silylethyl)-oligosulphide as claimed in claim 5.

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