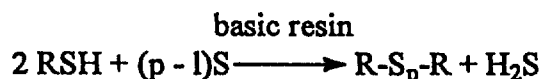


SYNTHESIS OF ORGANIC DISULPHIDES AND POLYSULPHIDES ✓

The present invention relates to organic disulphides and polysulphides of formula $R-S_p-R$ (in which $p \geq 2$) and more particularly to their production by reaction of mercaptans with sulphur, in the presence of
5 basic resins which act as catalysts, according to the reaction:



In the presence of such basic resins, organic disulphides and polysulphides of low sulphur order can be converted into polysulphides of higher sulphur order by
10 reaction with sulphur. Similarly, in the presence of such basic resins, organic polysulphides of high sulphur order can be converted into polysulphides of lower sulphur order by reaction with mercaptans.

Thus, European patent specification EP-A-
15 337,837 teaches the preparation of organic disulphides and polysulphides catalysed by organic anion exchange resins containing tertiary amine or quaternary ammonium functional groups (active in hydroxide form). Such
20 resins, generally in the form of grains or beads which are insoluble in liquid reaction media and are thus easy to separate out at the end of the reaction, allow organic disulphides and polysulphides to be obtained by reaction of elemental sulphur with mercaptans and also allow
25 organic polysulphides of high sulphur order to be obtained by reaction of elemental sulphur with organic polysulphides of lower sulphur order.

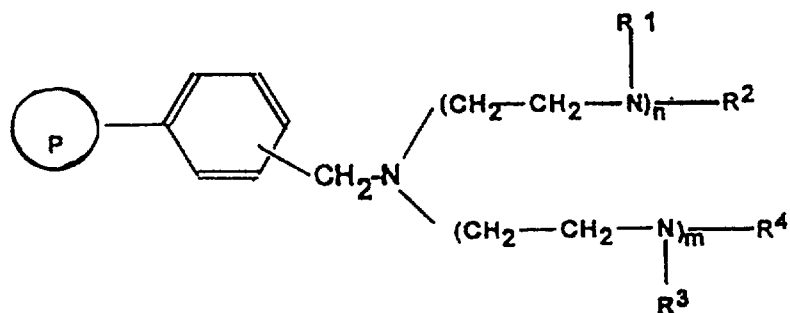
According to French patent specification FR 2,742,144, the use of basic resins containing a primary amine function makes it possible, when compared
30 with resins containing a tertiary amine function, to obtain a better degree of conversion of the reactants and/or a faster rate of reaction.

Similarly, French patent specification FR 2,742,145 recommends the use of strongly basic resins containing a guanidine or amidine function, which also makes it possible, when compared with resins containing a tertiary amine function, to obtain a better degree of conversion of the reactants and/or a faster reaction rate.

The aim of the present invention is to further improve these results in order to obtain a better degree of conversion of the reactants and/or a faster reaction rate.

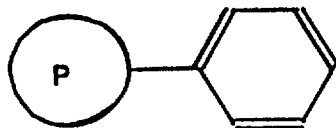
This aim is achieved by the use of resins functionalized with ethylenediamine or polyethylenepolyamine groups.

According to the present invention, there is provided a process for the preparation of an organic disulphide or polysulphide of formula $R-S_p-R$, in which each R, which may be the same or different, represents an organic group and $p \geq 2$, which process comprises reacting sulphur with a mercaptan of formula $R-SH$ or a polysulphide of lower sulphur order to convert it into polysulphide of higher order, or reacting a mercaptan with an organic polysulphide of high sulphur order to convert it into polysulphide of lower sulphur order, in the presence, as catalyst, of a resin based on polystyrene-divinylbenzene (PS-DVB) functionalized with ethylenediamine or poly-ethylenepolyamine groups and represented by the general formula (I):



(I)

in which:



5

represents the PS-DVB resin support,

each of R^1 , R^2 , R^3 and R^4 , which may be the same or different, represents a hydrogen atom or an alkyl, cycloalkyl, aryl or arylalkyl radical,

10

n is an integer of from 1 to 6, and

m does not exceed n and is 0 or an integer up to 5.

15

The resins which may suitably serve as starting materials for the preparation of the resins containing an ethylenediamine or polyethylenepolyamine function of general formula (I) can be PS-DVB copolymers or chloromethyl PS-DVB copolymers which, by appropriate chemical reactions described below, are converted into resins containing an ethylenediamine or polyethylene-

20

polyamine function according to the invention. With a low content of divinylbenzene (0.5 to 7% by weight) as crosslinking agent, copolymers of the gel type are obtained, whereas with higher DVB contents, macrocrosslinked resins of macroporous structure can be obtained. The DVB content can be from 0.5% to 60% by weight relative to the total weight of the PS-DVB copolymer.

25

Preferably, the starting materials and, consequently, the resins of general formula (I) are macrocrosslinked and of macroporous structure, since these characteristics entail better catalytic activity than is the case with resins of gel type.

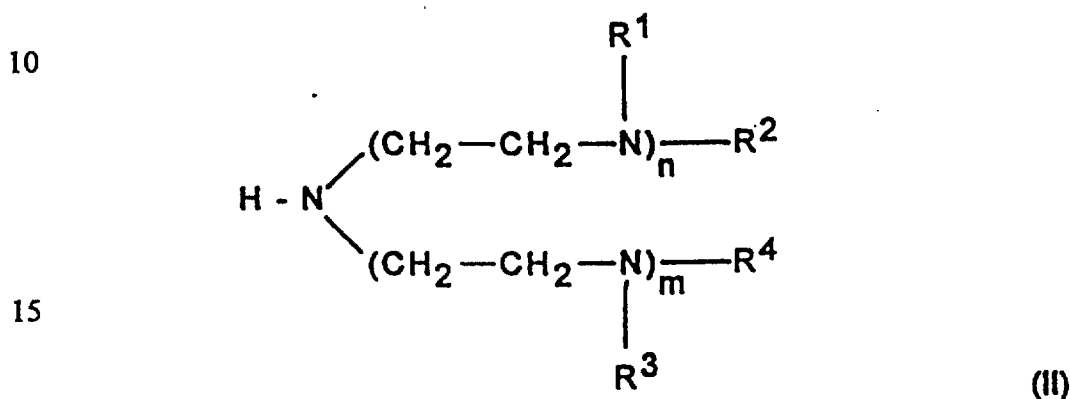
30

These PS-DVB resins can be chloromethylated with chloromethyl ether, according to known techniques which are described in the literature, to variable

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chlorine contents generally ranging from 1 to 20% by weight of chlorine relative to the weight of chloromethyl resin.

The resins according to the invention can be prepared, according to known amination techniques described in the literature, by reaction of a chloromethyl PS-DVB resin with ethylenediamine or a polyethylenepolyamine of general formula (II):



in which m, n, R¹, R², R³ and R⁴ are as defined above. In general, an excess of the amine (II) is dissolved in a solvent for swelling the chloromethyl resin (for example tetrahydrofuran); the chloromethyl resin is introduced into this solution and the reaction mixture is stirred for a period ranging from a few hours to several days (generally from 4 hours to 4 days) at a temperature which can range from about 20°C to the boiling point of the solvent, but must not exceed the stability limit temperature of the resin (generally 100°C). At the end of the reaction, the resin is washed with sodium hydroxide and then with a solvent of low boiling point (for example acetone) in order to help it to dry.

Preferably, an amine of formula (II) is used, in which n is an integer of from 1 to 5, m is 0 and R¹, R² and R⁴ are hydrogen atoms.

The radicals R of the organic mercaptans, disulphides and polysulphides may be hydrocarbon

radicals, generally alkyl, cycloalkyl, aryl, arylalkyl or alkylaryl groups. These radicals R can be substituted by one or more functional groups such as, for example, halogen atoms and -OH, -OR', -SR', NR'R'', -CN, -CHO, 5 -COR' and -COOR' groups, the symbols R' and R'' denoting C₁ to C₁₂ aliphatic radicals or cycloaliphatic, aromatic or alkylaromatic radicals.

The present invention applies in particular to the production of dialkyl disulphides and polysulphides 10 containing from 2 to 40 carbon atoms in total, such as, for example, dimethyl, diethyl, dipropyl, dibutyl, dipentyl, dihexyl, diheptyl, dioctyl, didecyl and didodecyl disulphides and polysulphides. It also applies to the preparation of cycloalkyl disulphides and 15 polysulphides such as, for example, dicyclohexyl disulphide and polysulphides, as well as to the preparation of aromatic disulphides or polysulphides, such as diphenyl disulphide and polysulphides.

The catalytic activity of the resins used in 20 the present invention appears at very low resin contents. Advantageously, the resin is present in an amount ranging from 0.01 to 20 parts by weight per 100 parts by weight of reaction mixture, including resin.

The process according to the invention 25 comprises a reaction which may be carried out at a temperature of from -10°C to 150°C. The temperature is preferably from +10°C to 120°C.

The reaction may be performed at atmospheric pressure or at higher pressures which may reach 50 bar. 30 In the case of relatively non-volatile reactants of low vapour pressure, the reaction may be performed at pressures below atmospheric pressure, optionally in the presence of an inert gas, such as nitrogen.

The mercaptan/sulphur molar ratio depends on 35 the nature of the mercaptan used and on the product to be

prepared (disulphide or polysulphide). Advantageously, this ratio is from 0.3 to 10 and preferably from 0.4 to 6.

5 When an organic polysulphide of high sulphur order is used at the start in order to convert it into organic polysulphide of low sulphur order, for example into a trisulphide $R-S_3-R$ or disulphide $R-S_2-R$ by the action of the corresponding mercaptan, a mercaptan/polysulphide molar ratio ranging from 2 to 10 is
10 advantageously used.

The production of organic disulphides or polysulphides in the presence of PS-DVB resins containing ethylenediamine or polyethylenepolyamine functions can be carried out in a stirred or tubular reactor, according to
15 a batchwise process, either by loading the reactants before reacting them, or by gradual addition of one of the reactants into the reactor, or alternatively according to a continuous process with controlled addition of the reactants.

20 In the case where sulphur is one of the reactants (the other being a mercaptan or a polysulphide of low sulphur order), it may be introduced in liquid or solid form.

The present invention is further described in
25 the following Examples which are included for purely illustrative purposes.

EXAMPLE 1 : Preparation of the resins according to the invention

30 A chloromethyl PS-DVB macroporous resin having the following characteristics was used:

- specific surface : 22.5 m²/g of dry resin
- average pore diameter : 2 nm
- pore volume : 0.69 ml/g
- 35 - mmol of chlorine/g of resin: 5.4 mmol/g of dry resin

10 g of dry chloromethyl resin (i.e. 54 mmol of chlorine) were weighed out and placed in contact, under a nitrogen atmosphere, with 6.48 g (108 mmol) of ethylenediamine diluted in 130 ml of tetrahydrofuran (THF) predried over molecular sieves. The reaction mixture thus obtained was stirred mechanically for 48 hours at 60°C.

After cooling to 20°C, the resin was filtered off and washed successively with THF, then with 20 ml of aqueous 10% sodium hydroxide solution, next with water until neutral and finally with acetone, before being dried under vacuum at 60°C to a constant weight.

A PS-DVB resin containing ethylenediamine functions (referred to hereinbelow as EDA resin) containing 7.6% by weight of nitrogen, i.e. 2.70 mmol of ethylenediamine per gram of dry resin, was thus obtained.

Working as above, but replacing the ethylenediamine with an equivalent molar amount of diethylenetriamine (11.2 g), of triethylenetetraamine (15.77 g), of tetraethylenepentaamine (20.41 g) or of pentaethylenehexamine (25.06 g), other resins according to the invention, identified as DETA, TETA, TEPA and PEXA respectively, were obtained. Their characteristics are collated in the following table.

The characteristics of PS-DVB resins according to the prior art, namely

- a resin containing tetramethylguanidine functions (referred to hereinbelow as TMG resin) prepared as above, but replacing the ethylenediamine with 12.5 g of tetramethylguanidine;

- a resin containing triazabicyclodecene functions (referred to hereinbelow as TBD resin) prepared as described on pages 23 and 24 of patent application FR 2,742,145, are also given in this table.

Resin	N%	mmol/g of dry resin
EDA	7.6	2.7 mmol of EDA/g
DETA	9.0	2.13 mmol of DETA/g
TETA	10.6	1.9 mmol of TETA/g
TEPA	11.8	1.68 mmol of TEPA/g
PEXA	11.6	1.38 mmol of PEXA/g
TMG	8.74	2.08 mmol of TMG/g
TBD	11.29	2.69 mmol of TBD/g

10 **EXAMPLE 2 : Synthesis of di(tert-dodecyl)**
trisulphide by reaction of tert-dodecyl mercaptan with
sulphur in the presence of basic resins

Tests for the production of bis(tert-dodecyl)
trisulphide were carried out under identical experimental
15 conditions, using the EDA, DETA, TETA, TEPA and PEXA
resins according to the invention as catalysts.

Comparative tests were also carried out using
the resins of the prior art, namely:

- Amberlyst A21 resin from Rohm & Haas, which
20 is a macroporous-type PS-DVB resin containing $-\text{CH}_2\text{N}(\text{CH}_3)_2$
functions, having a specific surface of $39.8 \text{ m}^2/\text{g}$ and 4.4
mmol of tertiary amine functions/g of dry resin;

- Purolite A109 resin, which is a
macrocrosslinked PS-DVB resin of macroporous structure
25 containing $-\text{CH}_2\text{NH}_2$ functions (4.3 mmol of NH_2/g of dry
resin);

- the TMG and TBD resins according to patent
application FR 2,742,145.

These tests were carried out in apparatus
30 comprising a 250 ml glass jacketed reactor equipped with:

- a sinter before the drainage valve,
- an inlet for introducing nitrogen via a dip
tube ending with a sinter (flow rate of nitrogen
controlled by a ball flowmeter),

35 - a water-cooled condenser connected to the

fume cupboard vacuum via a bubble counter containing oil,
- a thermostatically regulated bath allowing
oil to be circulated in the jacket,

- a glass stirrer ending with a PTFE anchor-
5 paddle and fitted with a stirrer motor with a tachometer,
- a thermometer probe in a glass sheath.

After the reactor had been placed under a
nitrogen atmosphere, 6 g or 15 g of resin (i.e. a
catalyst/RSH ratio = 4% or 10% respectively) were
10 introduced therein, followed by 151.2 g (750 mmol) of
tert-dodecyl mercaptan (TDM). The reactor was then heated
to 90°C, after which 24 g (750 mmol) of sulphur were
added in a single portion. With the stirring continuing
at 500 rev/min, the sulphur dissolved in about 30
15 minutes.

After switching on the nitrogen bubbling (flow
rate = 12 l/h) for the entire duration of the reaction,
samples were taken over time ($t = 0$ at the time of
introduction of the sulphur) in order to determine the
20 residual mercaptan content (% by mass) by argentimetry
and the free sulphur content by HPLC; the residual
mercaptan content makes it possible to determine the
degree of conversion of the TDM.

At the end of the reaction, the polysulphide is
25 filtered while hot (40°C) through the reactor sinter and
the resin is ready to be reused with a fresh load of TDM
and sulphur.

The results obtained with the various resins
are collated in the following table.

Test No.	Resin	% catalyst	Conversion of the TDM after reaction for 4 hours (%)
1	A-21	4	65
2	"	10	69
3	A-109	4	68
4	"	10	73
5	TMG	4	74
6	TBD	4	73
7	EDA	4	80
8	"	10	88
9	DETA	4	82
10	"	10	89
11	TETA	4	86
12	"	10	90
13	TEPA	4	86
14	PEXA	4	86

Examination of these results shows that the resins containing ethylenediamine or polyethylenepolyamine functions according to the invention (Tests 7 to 14) have higher activity than resins containing tertiary amine functions (Tests 1 and 2), primary amine functions (Tests 3 and 4) or guanidine functions (Tests 5 and 6).

EXAMPLE 3 : Synthesis of bis(tert-dodecyl) pentasulphide by reaction of tert-dodecyl mercaptan with sulphur in the presence of basic resins

6 g of resin (i.e. a catalyst/RSH ratio = 4%) were introduced into the reactor, placed beforehand under a nitrogen atmosphere, followed by 151.2 g (750 mmol) of TDM, in the same apparatus as in Example 2. After bringing the reactor to 90°C, 48 g (1.5 mol) of sulphur were introduced therein in three portions with intervals of 10 minutes. With the stirring maintained at 500 rev/min, the sulphur dissolved completely in about 45 minutes.

After switching on the nitrogen bubbling (flow rate = 6 l/h) for the entire duration of the reaction,

the process was then carried out as in Example 2. The test results are collated in the following table.

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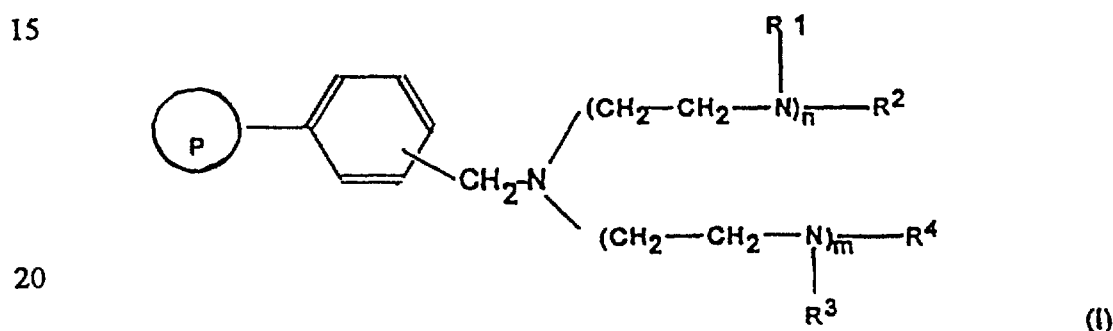
Test No.	Resin	Conversion of TDM after:	
		1 hour	3 hours
15	A-21	86%	97%
16	TMG	-	91%
17	A-109	-	95%
18	DETA	94%	99%

10

Examination of this table shows that the resin according to the invention (Test 18) gives better results than the resins of the prior art (Tests 15 to 17).

CLAIMS

1. A process for the preparation of an organic disulphide or polysulphide of formula $R-S_p-R$, in which each R, which may be the same or different, represents an organic group and $p \geq 2$, which process comprises reacting sulphur with a mercaptan of formula $R-SH$ or a polysulphide of lower sulphur order to convert it into polysulphide of higher order, or reacting a mercaptan with an organic polysulphide of high sulphur order to convert it into polysulphide of lower sulphur order, in the presence, as catalyst, of a resin based on polystyrene-divinylbenzene (PS-DVB) functionalized with ethylenediamine or polyethylenepolyamine groups and represented by the general formula (I):



in which:



represents the PS-DVB resin support,

each of R^1 , R^2 , R^3 and R^4 , which may be the same or different, represents a hydrogen atom or an alkyl, cycloalkyl, aryl or arylalkyl radical,

30 n is an integer of from 1 to 6, and

m does not exceed n and is 0 or an integer up to 5.

2. A process according to Claim 1, in which the resin of formula I is a macrocrosslinked resin of macroporous structure.

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3. A process according to Claim 1 or 2, in which the radicals R of the organic mercaptans, disulphides and polysulphides are alkyl, cycloalkyl, aryl, arylalkyl or alkylaryl groups unsubstituted or substituted by one or more functional groups.

4. A process according to any one of Claims 1 to 3, in which the resin is present in an amount of from 0.01 to 20 parts by weight per 100 parts by weight of reaction mixture, including resin.

5. A process according to any one of Claims 1 to 4, in which the reaction is carried out at a temperature of between -10°C and 150°C .

6. A process according to Claim 5, in which the reaction is carried out at a temperature of between $+10^{\circ}\text{C}$ and 120°C .

7. A process according to any one of Claims 1 to 6 for the preparation of a disulphide or polysulphide from a mercaptan and sulphur, in which the mercaptan/sulphur molar ratio is between 0.3 and 10.

8. A process according to Claim 7, in which the mercaptan/sulphur molar ratio is between 0.4 and 6.

9. A process according to any one of Claims 1 to 6, for the preparation of an organic polysulphide of low sulphur order from an organic polysulphide of high sulphur order and a mercaptan, in which the mercaptan/polysulphide molar ratio is from 2 to 10.

10. A process according to any one of the preceding Claims, in which the resin support is a chloromethyl PS-DVB resin.

11. A process according to Claim 1 substantially as described in Example 2 or 3.

12. An organic disulphide or polysulphide of formula $\text{R-S}_p\text{-R}$ (in which $p \geq 2$) prepared by the process claimed in any one of the preceding claims.

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