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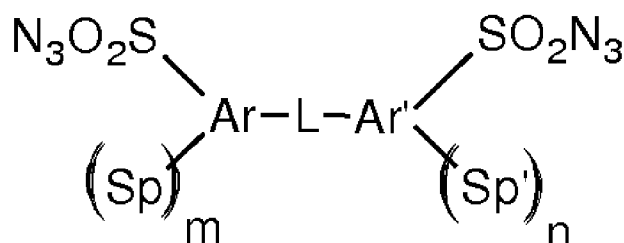
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(54) Title: NON EXPLOSIVE BIS-SULFONYL AZIDES



(II)

(57) Abstract: The invention relates to a compound of the general formula (I) $\text{N}_3\text{O}_2\text{S}-\text{Ar}-\text{L}-\text{Ar}'-\text{SO}_2\text{N}_3$, wherein: Ar and Ar' are aromatic building blocks; and L is a linking group comprising at least one heteroatom as well as an organic chain denoted as Sp'' and having at least two carbon atoms. The invention also relates to a compound of the general formula (II) wherein: Ar and Ar' are aromatic building blocks; L is a covalent bond or a linking group; m and n are both 0 or 1, at least one of m and n being 1; Sp and Sp' are organic chains having at least two carbon atoms. The invention also relates to the use of these compounds as cross linking agents in the manufacture of polymers.

5

NON EXPLOSIVE BIS-SULFONYL AZIDES**FIELD OF THE INVENTION**

10 The present invention relates to a class of sulfonyl azide compounds used as crosslinking agents and having non explosive properties.

TECHNICAL BACKGROUND

15 Chemical crosslinkers such as organic peroxides and silanes are able to link polymer chains, so as to create three-dimensional polymer networks. Crosslinking reactions lead to superior material characteristics of the polymers compared to the corresponding non-crosslinked raw polymers.

 In particular, thermoplastic polyolefins and elastomers are polymers which are frequently modified by crosslinking in order to improve their rheological properties such as melt strength and their general processability.
20 The physical properties of the crosslinked polymers, for example specific molecular weight distribution, tensile and tear strength, and snappiness are generally improved.

 Peroxide-based crosslinking processes are radical processes which are difficult to control and generate decomposition byproducts. Silane-based
25 processes are two-step processes also initiated by a radical peroxide reaction to graft a silane to a polymer. The second step is then the crosslinking reaction which involves the hydrolysis of alkoxy groups.

 Azide compounds, and more particularly bis sulfonyl azide compounds,
30 are known as advantageous crosslinkers in the art.

 A sulfonylazide coupling process relies on the thermal decomposition of the sulfonylazide, which generates reactive nitrenes that in the singlet state are known to undergo carbon-hydrogen (C-H) insertion to form sulfonylamido linkages. This process can be controlled by process temperature and
35 concentration of the azide. The main advantages of sulfonylazide crosslinking versus radical crosslinking are a better processability (control of the reaction, no adverse effect on flow rate), less byproducts and a more homogeneous crosslinking of the polymers (resulting in better mechanical properties).

For example, document GB 1129399 describes the production of polymer fibers with the use of crosslinkers, such as bis azides. Sulfonyl azides and azido formates are mentioned, in particular 1,10-decane bis(sulfonazide) and 4,4'-diphenylether bis(sulfonazide).

5 Document US 3,298,975 relates to partially foamed polypropylene compositions including sulfonyl azides as crosslinkers. A novel synthesis of a chloroaliphatic poly(sulfonyl azide) is described, but non-chlorinated alkane bis(sulfonyl azides) are also mentioned, such as 1,6-bis(4-azidosulfonylphenyl)hexane.

10 Documents US 3,352,798 and GB 1080619 relate to the use of poly(sulfonyl azides) as crosslinkers for a broad range of polymers. Aralkylene and some sulfonyl azide compounds including ether groups are mentioned.

Documents BE 638643, BE 638644 and BE 622066 relate to the production of polypropylene foams or hollow polypropylene plastic, using sulfonyl azide or azidoformate crosslinkers similar to the ones mentioned in
15 the other documents above.

One important disadvantage of most of the above chemical sulfonylazide crosslinking systems is that the crosslinkers are explosive. Therefore, they have to be used with phlegmatizing agents, which makes the crosslinking process more expensive. In addition, phlegmatizing agents are
20 not easy to handle, require precise industrial adjustments, and are not desirable in every application.

For instance, DPO-BSA (4,4'-diphenylether-bis(sulfonazide)) is a well-known bis-sulfonyl azide crosslinker currently used in the industry for polymer manufacturing or post-treatment. But it has the disadvantage of being explosive according to two tests of the UN-manual for tests and criteria and the (German) explosives act (shock sensitive and explosive at heating under partial confinement in the Koenen-test). This compound needs to be phlegmatized with an inert non-explosive substance (phlegmatizing agent) for
25 transportation, safe handling and technical use, for example in extrusion processes. A typical phlegmatized composition contains less than 67%(w/w) DPO-BSA and more than 33% (w/w) stabilizer, such as Irganox® 1010. Phlegmatizing agents have to be adjusted to the plastics manufacturing process, requiring development and testing of every new combination.

35 There is therefore a need for non or less explosive crosslinkers, with no need or less need for phlegmatization, such crosslinkers being advantageously synthesized in an easy way. Non or less explosive

crosslinkers would also result in reduced costs of synthesis, formulation and transportation.

SUMMARY

5 It is a first object of the invention to provide a compound of the general formula



wherein:

- Ar and Ar' are aromatic building blocks; and
- 10 - L is a linking group comprising at least one heteroatom as well as an organic chain denoted as Sp'' and having at least two carbon atoms.

According to one embodiment, the at least one heteroatom in the linking group L is selected from sulfur, nitrogen, and oxygen.

15 According to one embodiment, the organic chain Sp'' is an aliphatic chain, and is preferably linear.

According to one embodiment, the organic chain Sp'' comprises from 2 to 20 carbon atoms, preferably from 6 to 16 carbon atoms.

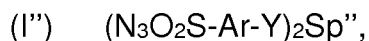
20 According to one embodiment, Ar is a phenyl group, or Ar' is a phenyl group, and preferably Ar and Ar' are both phenyl groups, said phenyl groups being substituted or not.

According to one embodiment, L is Y-Sp''-Y', wherein:

- Y and Y' are both functional groups comprising a heteroatom, which are preferably independently selected from -O-, -NH-, -NR-,
25 -OC(=O)NH-, -OC(=O)NR'-, -OC(=O)O-, -NHC(=O)NH-,
-NHC(=O)O-, -NHC(=O)NR'-, -NRC(=O)NH-, -NRC(=O)O-,
-NRC(=O)NR'-, -S-, -SO₂-, -C(=O)O-, -C(=O)NH-, -C(=O)NR-,
-C(=O)-, -OC(=O)-, -NHC(=O)- and -NRC(=O)-, R and R' being alkyl or aryl groups; and
- 30 - Sp'' is as defined above.

According to one embodiment, Ar and Ar' are phenyl groups, substituted or not; L is O-Sp''-O; and the organic chain Sp'' is an aliphatic chain which preferably comprises at least 3, preferably at least 4, more preferably at least 5, and most preferably at least 6 carbon atoms.

35 According to one embodiment, the compound has the general formula:



wherein Ar, Y and Sp'' are as defined above.

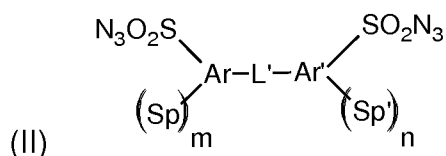
According to one embodiment, the compound is 1,6-bis-(4-azidosulfonylphenoxy)-hexane.

According to one embodiment, the compound is 1,10-bis-(4-azidosulfonylphenoxy)-decane.

5 According to one embodiment, the compound is 1,2-bis-(4-azidosulfonylphenoxy)-hexadecane.

According to one embodiment, the compound is an isomeric mixture of 4,8-bis-(4-azidosulfonylphenoxy)-tricyclo[5.2.1.0^{2,6}]decane.

10 It is a second object of the invention to provide a compound of the general formula



wherein:

- Ar and Ar' are aromatic building blocks;
- 15 - L' is a covalent bond or a linking group;
- m and n are both 0 or 1, at least one of m and n being 1;
- Sp and Sp' are organic chains having at least two carbon atoms.

According to one embodiment, L' comprises at least one heteroatom, preferably selected from sulfur, nitrogen, and oxygen.

20 According to one embodiment, m is 1 and n is 0; or m is 0 and n is 1.

According to one embodiment, Sp and/or Sp' is an aliphatic chain, and is preferably linear.

According to one embodiment, Sp and/or Sp' comprises from 2 to 20 carbon atoms, preferably from 6 to 18 carbon atoms.

25 According to one embodiment, L' is selected from -O-, -NH-, -NR-, -OC(=O)NH-, -OC(=O)NR'-, -OC(=O)O-, -NHC(=O)NH-, -NHC(=O)O-, -NHC(=O)NR'-, -NRC(=O)NH-, -NRC(=O)O-, -NRC(=O)NR'-, -S-, -SO₂-, -C(=O)O-, -C(=O)NH-, -C(=O)NR-, -C(=O)-, -OC(=O)-, -NHC(=O)- and -NRC(=O)-, R and R' being alkyl or aryl groups.

30 According to one embodiment, L' is -O-, Ar and Ar' are phenyl groups, and Sp and/or Sp' is an aliphatic chain comprising at least 3, preferably at least 4, more preferably at least 5 and most preferably at least 6 carbon atoms.

According to one embodiment, the compound is 4,4'-bis-(azidosulfonyl)-3-pentadecyl diphenylether.

35 It is another object of the invention to provide a process for producing any of the abovementioned compounds, which comprises providing starting

compounds A and B, wherein A and B are substituted aromatic compounds, and which comprises a step of reacting A and B.

According to one embodiment, this process is for producing a compound according to the first object of the invention, wherein the starting
5 compounds A and B are reacted in the presence of an additional compound Z-Sp''-Z', Sp'' being the organic chain defined above, and Z and Z' being two reactive groups ; and wherein A and B are preferably identical.

According to one embodiment, this process is for producing a compound according to the second object of the invention, wherein the step of
10 reacting A and B is followed by a step of chlorosulfonating the obtained product, and then a step of reacting the obtained product with sodium azide.

It is another object of the invention to provide a composition comprising the compound according to any one of claims 1 to 20, and containing at most 50% (w/w), preferably at most 40% (w/w), more preferably at most 30% (w/w),
15 even more preferably at most 20% (w/w), most preferably at most 10% (w/w) of a phlegmatizing agent.

It is another object of the invention to provide the use of any of the abovementioned compounds, as a crosslinker.

According to one embodiment, said compound is used with at most 50%
20 (w/w), preferably at most 40% (w/w), more preferably at most 30% (w/w), even more preferably at most 20% (w/w), most preferably at most 10% (w/w) of a phlegmatizing agent.

According to one embodiment, said compound is used without any phlegmatizing agent.

25 According to one embodiment, this use is a use as a crosslinker in the manufacture of polyolefins, polyolefin copolymers and blends of polyolefins, preferably in the manufacture of polypropylene or polyethylene.

According to one embodiment, this use is a use as a crosslinker in the manufacture of elastomers, elastomer copolymers and blends of elastomers,
30 preferably in the manufacture of EPM, EPDM and EPM-polyolefin blends.

The present invention overcomes the disadvantages of prior art. It more particularly provides new crosslinking agents that are not explosive or are less explosive than prior art compounds, and thus do not require a phlegmatizing agent, or at least require smaller amounts of phlegmatizing agent.

35 Without wishing to be bound by any theory, the inventors believe that this is accomplished thanks to the integration of additional carbon atoms in a spacer or side chain in a bis(aryl sulfonyl azide) molecule. The increase in molecular weight achieved owing to the spacer or side chain is believed to

result in reduced or suppressed explosiveness. Furthermore, reduced crystallinity is believed to be present in the compounds of the invention, also resulting in reduced or suppressed explosiveness as no large crystals are formed in the manufacturing process.

5 In particular, the compounds of the present invention have reduced explosiveness relative to DPO-BSA, which is one important sulfonylazide crosslinker currently used in the industry.

The spacer can be positioned between the two aryl sulfonyl azide groups, or it can be positioned as a substituent or side chain on one or both of
10 the aryl sulfonyl azide groups.

Furthermore, the compounds of the invention are relatively easy to synthesize, in particular when one or more heteroatoms are present in the linker between the two aryl sulfonyl azide groups. This stands in contrast with compounds mentioned in the prior art such as 1,6-bis(4-
15 azidosulfonylphenyl)hexane, which are believed to be more difficult to synthesize.

DETAILED DESCRIPTION

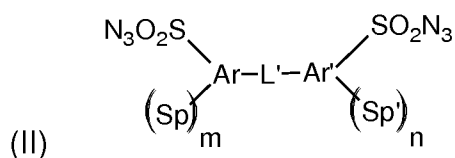
The invention will now be described in more detail without limitation in
20 the following description.

The compounds of the invention fall into two categories, namely type 1 and type 2.

Compounds of the invention of type 1 have following general formula:



25 Compounds of the invention of type 2 have following general formula:



In the above formulas, Ar and Ar' are aromatic building blocks.

30 The aromatic building blocks Ar and Ar' are aryl moieties, *i.e.* they are or they comprise respective aromatic rings. These aromatic rings can be substituted or not. In case substituents are present, they can in particular be similar to the side chains Sp and Sp' which are described in more detail below. In this case, the aromatic ring of the Ar / Ar' aromatic building block can be
35 linked to more than one side chain Sp / Sp', for instance to two side chains

Sp / Sp', or to three side chains Sp / Sp', or to four side chains Sp / Sp', including the one shown in formula (II). The various side chains Sp / Sp' linked to the aromatic ring can be identical or different.

Ar and Ar' can be identical or different, preferably identical. Still preferably, Ar and Ar' are phenyl groups. Alternatively, they can be naphthyl groups.

In formula (I), L is a linking group or linker.

The linking group L comprises at least one heteroatom and a spacer denoted as Sp''.

The heteroatom is preferably sulfur, nitrogen, or oxygen.

In formula (II), L' is either a covalent bond or a linking group; m and n are each independently 0 or 1; and Sp and Sp' are side chains – which can also be called spacers in the context of this application.

When m=0, Sp is not present, whereas when m=1, Sp is present.

When n=0, Sp' is not present, whereas when n=1, Sp' is present.

At least one of Sp and Sp' is present, which means that at least one of m and n is 1. According to one embodiment, only one of Sp and Sp' is present. According to an alternative embodiment, both Sp and Sp' are present, in which case they can be identical or different.

In both of the above formulas, Sp, Sp' and Sp'' are organic chains. In particular each of Sp, Sp' and Sp'' can be an aromatic chain or an aromatic group-containing chain. However, preferably, each of Sp, Sp' and Sp'' is an aliphatic chain. Each of Sp, Sp' and Sp'' preferably comprises at least two carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 2 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 3 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 4 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 5 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 6 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 7 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 8 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 9 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 10 carbon atoms.

5 According to one embodiment, the chain Sp or Sp' or Sp'' has 11 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 12 carbon atoms.

10 According to one embodiment, the chain Sp or Sp' or Sp'' has 13 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 14 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 15 carbon atoms.

15 According to one embodiment, the chain Sp or Sp' or Sp'' has 16 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 17 carbon atoms.

20 According to one embodiment, the chain Sp or Sp' or Sp'' has 18 carbon atoms.

According to one embodiment, the chain Sp or Sp' or Sp'' has 19 carbon atoms.

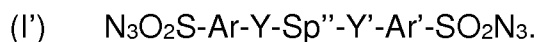
According to one embodiment, the chain Sp or Sp' or Sp'' has 20 carbon atoms.

25 According to one embodiment, the chain Sp or Sp' or Sp'' has more than 20 carbon atoms.

30 The chain Sp or Sp' or Sp'' may be linear, branched or cyclic. It can be saturated or unsaturated and is most preferably saturated. It can be substituted or, more preferably, non-substituted. In case it is substituted, alkyl chain substituents are preferred, as they contribute to a reduced tendency to explosiveness.

35 The compounds of the invention can be both of type 1 and type 2 at the same time. Such compounds can be compounds of formula (I), wherein at least one of Ar and Ar' comprises an aromatic ring with a respective chain Sp or Sp' as defined above linked to said aromatic ring. Such compounds can also be compounds of formula (II), wherein L' is a linking group similar to a linking group L of formula (I) defined above.

Preferred compounds of type 1 are of the general formula:



In this formula, Sp'' is as defined above; Y and Y' are two functional groups which can be identical or different. Preferably, the two groups N₃O₂S-Ar-Y- and N₃O₂S-Ar'-Y'- respectively linked to the spacer Sp'' are identical.

5 Such compounds are of the general formula:



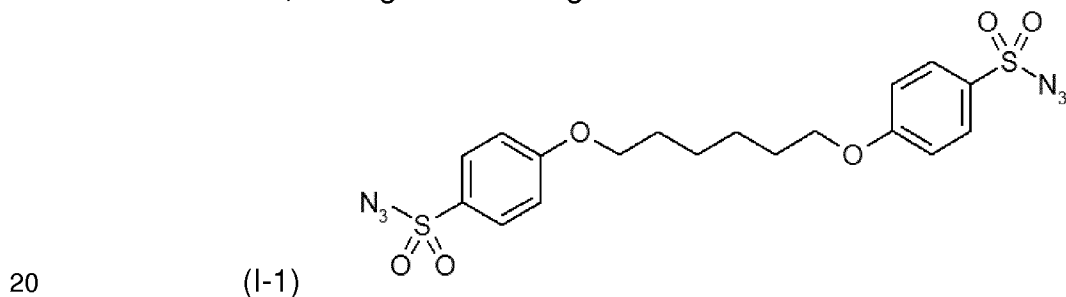
The functional groups Y and Y' advantageously comprise at least one heteroatom, preferably selected from sulfur, oxygen, and nitrogen.

They are more preferably selected from the following groups: -O-,
 10 -NH-, -NR-, -OC(=O)NH-, -OC(=O)NR'-, -OC(=O)O-, -NHC(=O)NH-,
 -NHC(=O)O-, -NHC(=O)NR'-, -NRC(=O)NH-, -NRC(=O)O-, -NRC(=O)NR'-,
 -S-, -SO₂-, -C(=O)O-, -C(=O)NH-, -C(=O)NR-, -C(=O), -OC(=O)-, -NHC(=O)-
 and -NRC(=O)-, wherein R and R' are alkyl or aryl groups.

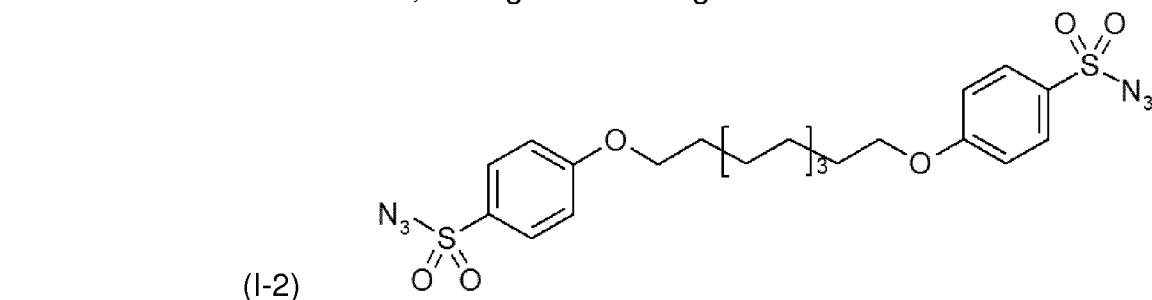
More preferably, R and R' are selected from the methyl, ethyl, propyl,
 15 isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, pentyl, isoamyl, 4-methyl-2-
 pentyl, 2-ethylhexyl, and phenyl groups.

Preferred examples of compounds of type 1 are:

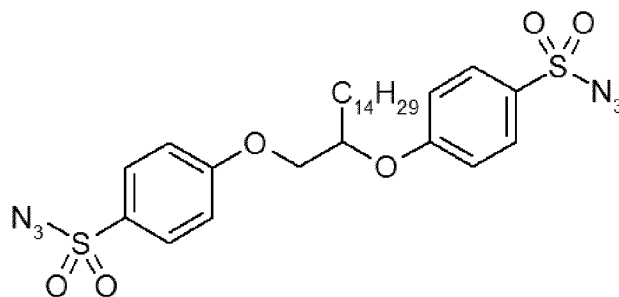
- 1,6-bis-(4-azidosulfonylphenoxy)-hexane, also designated POHOP-SA, having the following formula:



- 1,10-bis-(4-azidosulfonylphenoxy)-decane, also designated PODOP-SA, having the following formula:

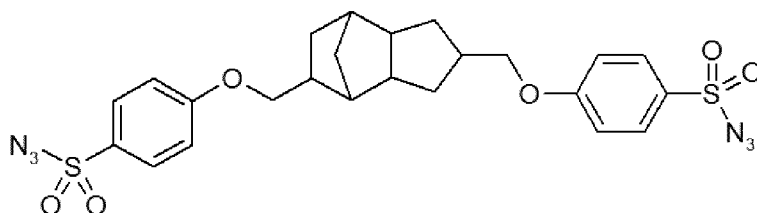


- 1,2-bis-(4-azidosulfonylphenoxy)-hexadecane, also designated POTDEOP-SA, having the following formula:



(I-3)

- 4,8-bis-(4-azidosulfonylphenoxy)methyl-tricyclo[5.2.1.0^{2,6}]decane (isomeric mixture), also designated POTCOP-SA, having the following formula:



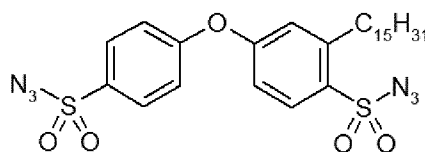
(I-4)

Preferably, in the compounds of the invention of type 2, L' is a functional group, advantageously comprising a heteroatom such as sulfur, nitrogen or oxygen. More preferably Y'' is selected from the following groups: -O-, -NH-, -NR-, -OC(=O)NH-, -OC(=O)NR'-, -OC(=O)O-, -NHC(=O)NH-, -NHC(=O)O-, -NHC(=O)NR'-, -NRC(=O)NH-, -NRC(=O)O-, -NRC(=O)NR'-, -S-, -SO₂-, -C(=O)O-, -C(=O)NH-, -C(=O)NR-, -C(=O)-, -OC(=O)-, -NHC(=O)-, and -NRC(=O)-, wherein R and R' are alkyl or aryl groups.

More preferably, R and R' are selected from the methyl, ethyl, propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, pentyl, isoamyl, 4-methyl-2-pentyl, 2-ethylhexyl, and phenyl groups.

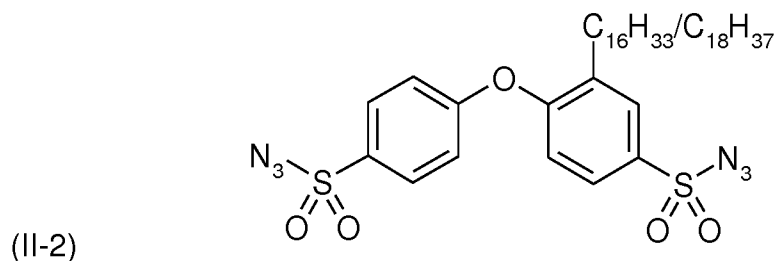
Preferred examples of a compound of type 2 of the present invention are:

- 4,4'-bis-(azidosulfonyl)-3-pentadecyl diphenylether, also designated PBSA, of the following formula:



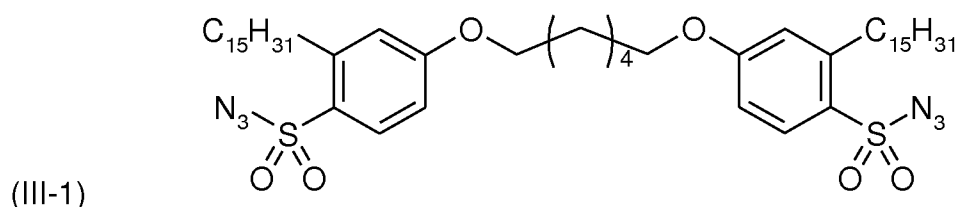
(II-1)

- a mixture of 2-fatty alkyl substituted DPO-BSA (*i.e.* a mixture of 4,4'-bis-(azidosulfonyl)-2-hexadecyl diphenylether and 4,4'-bis-(azidosulfonyl)-2-octadecyl diphenylether), also designated as H/ODPO-BSA, of the following formula:



A preferred example of a compound of a mixed type of the present invention (both type 1 and type 2) is:

- 1,6-bis-(4-azidosulfonyl-3-pentadecylphenoxy)hexane, also designated PDPOHOPDP-SA, of the following formula:

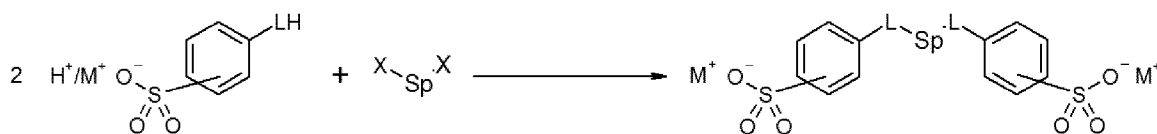


10

The compounds of the present invention can be prepared by reacting starting compounds A and B, optionally in the presence of an additional compound C. Compounds A and B are substituted aromatic compounds. They can be identical or different. They can bear sulfonylazide substituents. Alternatively, the sulfonylazide groups can be provided in one or more posterior reaction steps.

In particular, in order to produce compounds of type 1 having the above formula (I''), the starting compounds A and B are one and the same compound, and use can be made of a compound of formula Z-Sp''-Z as an additional compound C, wherein Sp'' is as defined above, and Z is a reactive functional group.

More specifically, some of the compounds of type 1 can be prepared according to so-called route 1, comprising the following first step:



25

In the above scheme, M^+ represents a metallic cation, such as for instance sodium or potassium. Sp is a spacer (denoted Sp'' above) and L has a different meaning from formula (I).

According to one embodiment, L is selected from O, NH, or NR, where
 5 R is an alkyl or an aryl group, as defined above, and X is selected from Cl, Br, I, -NCO, -OC(=O)Cl, and -NR'C(=O)Cl, where R' is an alkyl or an aryl group, as defined above.

According to another embodiment, LH is SH or S $\cdot$ M $^+$ and X is Cl, Br, or I.

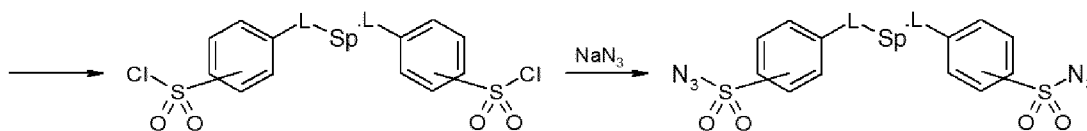
10 This reaction can be performed in the presence of an inorganic base such as MOH, M₂CO₃, or in the presence of an organic base.

In case L is S, it is possible to then oxidize this linking group into SO₂ *e.g.* by treatment of the sulfide with hydrogen peroxide.

The first step is then followed by a second step of reacting the obtained
 15 compound with a chlorination agent. The chlorination agent can be for instance selected from thionylchloride, sulfonylchloride, phosphorylchloride, phosgene, oxalyl chloride, preferably thionylchloride.

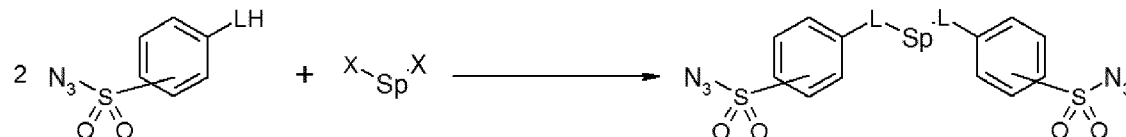
The second step is then followed by a third step of reacting the obtained sulfonyl chloride compound with an azide source, preferably sodium azide.

20 The second and third steps can be illustrated as follows:



Route 1 makes it possible to obtain compounds of formula (I''), wherein
 Y is -O-, -NH-, -NR-, -OC(=O)NH-, -OC(=O)NR'-, -OC(=O)O-, -NHC(=O)NH-,
 25 -NHC(=O)O-, -NHC(=O)NR'-, -NRC(=O)NH-, -NRC(=O)O-, -NRC(=O)NR'-,
 -S-, and -SO₂-.

The same compounds of type 1 can be prepared according to so-called route 2, comprising the following step:



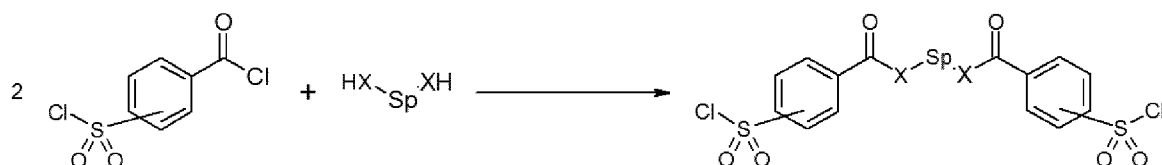
30

In the above scheme, LH, L, and X have the same meanings as in route 1. This reaction can be performed in the presence of an inorganic base such as MOH, M₂CO₃, or in the presence of an organic base.

Route 2 circumvents the need for any posterior chlorination or azidation step.

Other compounds of type 1 can be prepared according to so-called route 3, comprising the following first step:

5

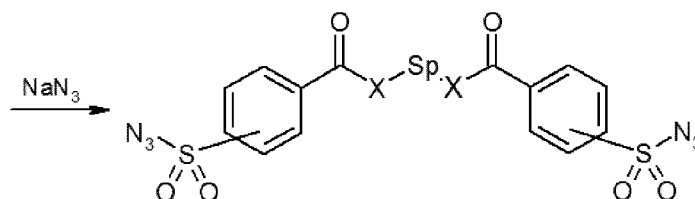


In the above scheme, X is O, NH, or NR, R being an alkyl or aryl group as defined above.

10 This reaction can be performed in the presence of an inorganic base such as MOH, M_2CO_3 , or in the presence of an organic base.

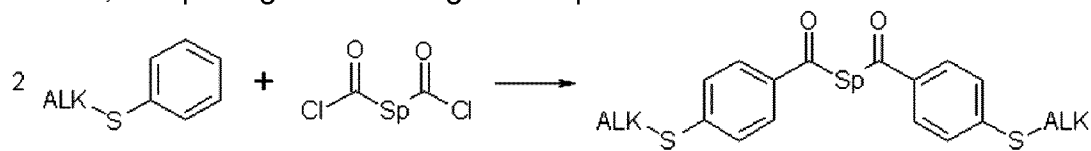
The first step is then followed by a second step of reacting the obtained compound with sodium azide. The second step can be illustrated as follows:

15



Route 3 makes it possible to obtain compounds of formula (I''), wherein Y is $-\text{C}(=\text{O})\text{O}-$, $-\text{C}(=\text{O})\text{NH}-$ or $-\text{C}(=\text{O})\text{NR}-$.

20 Other compounds of type 1 can be prepared according to so-called route 4, comprising the following first step:

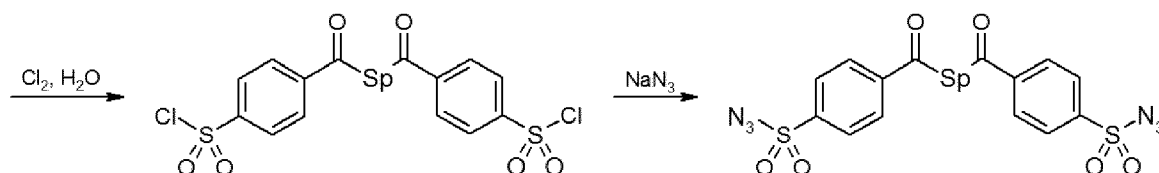


In the above scheme, ALK is an alkyl chain, such as a methyl group for instance.

25 This reaction can be performed in the presence of AlCl_3 or any other Lewis acid.

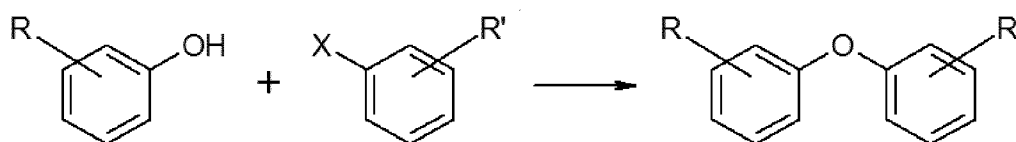
The first step is then followed by a second step of reacting the obtained compound with a mixture of Cl_2 and H_2O , and then by a third step of reacting the obtained sulfonyl chloride with an azide source like sodium azide. The second and third steps can be illustrated as follows:

30



Route 4 makes it possible to obtain compounds of formula (I''), wherein
 5 Y is -C(=O)-.

Some of the compounds of type 2 can be prepared according to so-called route 5, comprising the following first step:

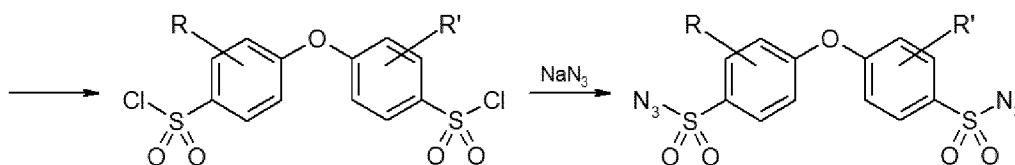


In this scheme, X is Cl, or Br, or I. R and R' are alkyl or aryl groups, as defined above. One of R and R' can be omitted; at least one of R and R' is or contains the above-defined spacer Sp or Sp'. Preferably, -R is -Sp-H or -R' is -Sp'-H.

This reaction step is preferably catalyzed by a transition metal catalyst, e.g. based on copper or palladium.

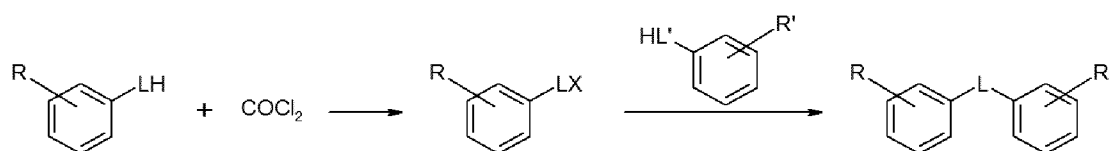
The first step is then followed by a second step of reacting the obtained compound with a chlorosulfonation agent. For instance, use may be made of at least four equivalents chlorosulfonic acid for direct chlorosulfonation, or at
 20 least two equivalents chlorosulfonic acid or sulfuric acid followed by a chlorination as described in route 1, or sulfurylchloride, etc.

The second step is then followed by a third step of reacting the obtained compound with an azide source like sodium azide. The second and third steps can be illustrated as follows:



Route 5 thus makes it possible to prepare compounds of type 2 wherein
 L' is -O-.

Some of the compounds of type 2 can be prepared according to so-called route 6, comprising the following first and second steps:



In this scheme, R and R' are alkyl or aryl groups, as defined above. One of R and R' can be omitted; at least one of R and R' is or contains the above-defined spacer Sp or Sp'. L has a different meaning from above in this scheme.

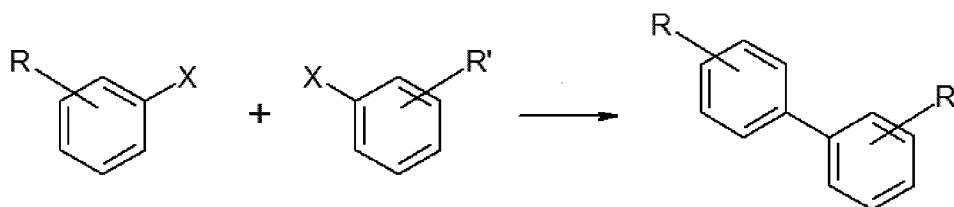
In the first step, LH is OH, NH_2 or $\text{-NR}''\text{H}$, where R'' is an alkyl or aryl group having the same general definition as R and R'.

In the second step, LX is -OC(=O)Cl , -N=C=O or $\text{-NR}''\text{C(=O)Cl}$, R'' being as defined above; and L'H is OH, NH_2 or $\text{-NR}'''\text{H}$, where R''' is an alkyl or aryl group having the same general definition as R and R'.

In the compound obtained at the second step, L has a different meaning and can be -OC(=O)O- , -OC(=O)NH- , $\text{-OC(=O)NR}'''\text{-}$, -NHC(=O)O- , $\text{-NR}''\text{C(=O)O-}$, -NHC(=O)NH- , $\text{-NHC(=O)NR}'''\text{-}$, $\text{-NR}''\text{C(=O)NH-}$ or $\text{-NR}''\text{C(=O)NR}'''\text{-}$, R'' and R''' being as defined above.

The second step is followed by a third step of chlorosulfonation and a fourth step of reacting with sodium azide, which are analogous to the second and third step of route 5.

Some of the compounds of type 2 can be prepared according to so-called route 7, comprising the following first step:

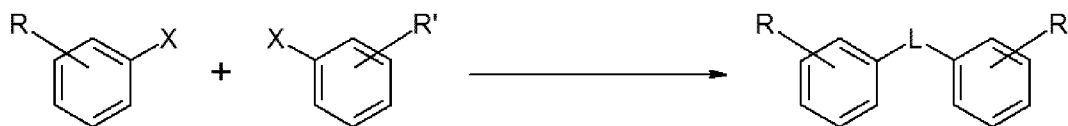


In this scheme, X is Cl, or Br or I; and R and R' are alkyl or aryl groups, as defined above. One of R and R' can be omitted; at least one of R and R' is or contains the above-defined spacer Sp or Sp'. This reaction step is preferably catalyzed with a transition metal catalyst, based e.g. on copper or palladium.

This first step is followed by a second step of chlorosulfonation and a third step of reacting with an azide source like sodium azide, which are analogous to the second and third step of route 5.

Route 7 makes it possible to obtain compounds of type 2, wherein L' in formula (II) is a covalent bond.

Some of the compounds of type 2 can be prepared according to so-called route 8, comprising the following first step:



5

In this scheme, X is Cl, or Br or I; and R and R' are alkyl or aryl groups, as defined above; and L is -S- or -SO₂-. The reaction is performed in the presence of a compound M₂S, where M is a metallic element (for instance sodium or potassium) and in the presence of a catalyst, preferably a transition metal catalyst, e.g. based on copper.

10

An oxidation step is then performed if the -SO₂- linking group is desired e.g. by treatment of the sulfide with hydrogen peroxide.

Then, a second step of chlorosulfonation and a third step of reaction with an azide source like sodium azide are performed, in an analogous manner as in route 5.

15

Route 8 makes it possible to obtain compounds of type 2, wherein L' in formula (II) is -S- or -SO₂-.

In order to prepare compounds of the invention where the aromatic building blocks Ar and Ar' are not based on phenyl groups but rather on different aryl groups, similar reaction routes may be employed by analogy.

20

One or more compounds of the invention can be formulated in a crosslinker composition. According to one embodiment, this crosslinker composition is devoid of any phlegmatizing agent. According to an alternative embodiment, this crosslinker composition comprises a phlegmatizing agent. A phlegmatizing agent is defined as an inert compound which reduces the explosiveness of the bissulfonylazide compound, according to the tests defined in the UN manual for tests and criteria.

25

Phlegmatizing agents can be organic or inorganic compounds. Organic compounds can be solvents or solids like e.g. Irganox® 1010. Inorganic compounds can be e.g. diatomaceous earth or silica gel.

30

The amount of phlegmatizing agent used in the present invention can be varied over a wide range, depending on how much phlegmatizing agent is required to ensure safe handling and use of the compounds of the invention and to allow a transport classification as non-explosive material. In particular, the amount of phlegmatizing agent in the compositions of the invention can be from 0 to 50% (w/w), preferably from 0 to 40% (w/w), more preferably from 0

35

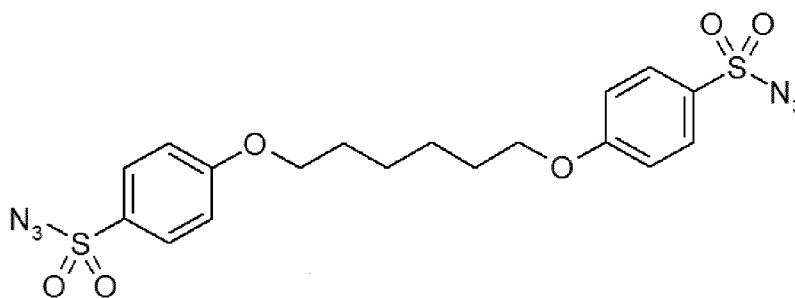
to 30% (w/w), even more preferably from 0 to 20% (w/w), and most preferably from 0 to 10% (w/w).

The compounds and compositions of the invention are useful in the manufacture of polymers such as polyolefins (in particular polypropylene and polyethylene), in the crosslinking of polymers, and in the manufacture of synthetic rubber.

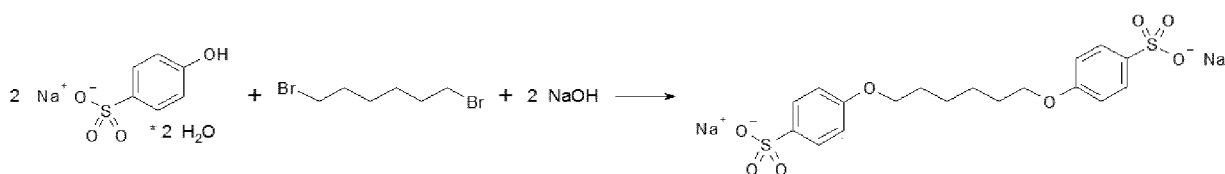
EXAMPLES

The following examples illustrate the present invention without limitation.

Example 1: synthesis of POHOP-SA



Step 1: 1,6-bis-(4-sulfophenoxy)-hexane disodium salt (POHOP-SONa)

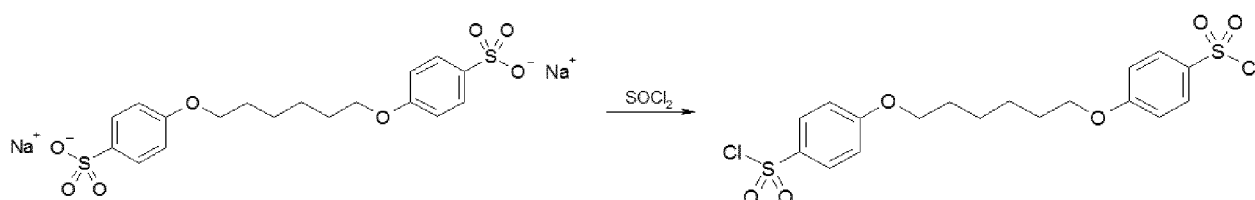


A solution of 320 sodium hydroxide in 480 g water was added slowly at 25°C to a solution of 1858 g sodium 4-hydroxybenzene sulfonate and 12.8 g tetrabutylammonium bromide in 3120 g water. To this mixture 976 g 1,6-dibromohexane was added within 1 h. The mixture was heated to 100°C and stirred for 15 h. The thick slurry was diluted with 400 ml water and stirred for another 7 h at 100°C. The suspension was diluted with 11.6 L water and stirred at 100°C for 8 h and then cooled to room temperature for filtration. The solids were washed with 4 L water followed by 4 L acetone and dried at 50°C. 1599 g of a white solid with an assay of 92.5% (w/w, HPLC) was isolated, with chemical yield of 80%.

Analytical data:

Melting point >345°C; ¹H-NMR (300 MHz in D₂O): 7.65 ppm (d, 4H), 6.97 ppm (d, 4H), 4.02 ppm (t, 4 H), 1.70 ppm (broad quintet, 4 H), 1.40 ppm (broad, 4 H).

5 Step 2: 1,6-bis-(4-chlorosulfonylphenoxy)-hexane (POHOP-SC)



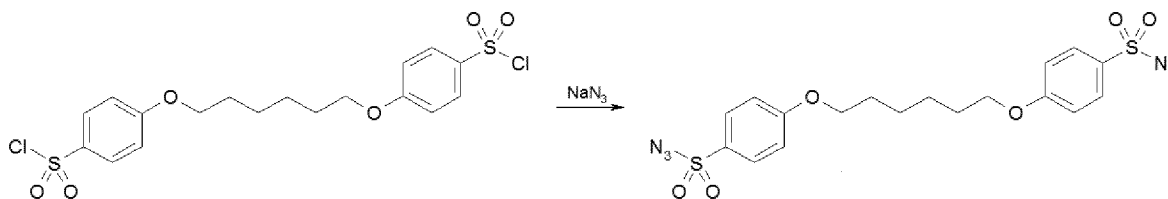
A mixture of 1471 g POHOP-SO₃Na, 7 kg thionyl chloride, and 7 g
10 dimethylformamide (DMF) was heated to 75°C for 17 h. 3.5 kg thionyl chloride
were removed by distillation at 50°C and 100 mbar and the distillation was
continued after the addition of three times each 2 L toluene until a distillation
residue of 2.3 kg was obtained. It was diluted with 1.5 L toluene and cooled to
17°C. The solids were filtered off and washed with 1.5 L toluene. The wet filter
15 cake was slurried in 2.5 L water in order to removed salts and residual traces
of thionyl chloride. The solids were filtered, washed with 2.5 L water, and dried
at 40°C. 1329 g of a white solid was obtained. The chemical yield based on
the mass of the product is 99%.

Analytical data:

20 Melting point: 126 – 128°C; ¹H-NMR (300 MHz in CDCl₃): 7.97 ppm (d,
4H), 7.05 ppm (d, 4H), 4.11 ppm (t, 4 H), 1.90 ppm (broad quintet, 4 H), 1.60
ppm (broad, 4 H).

Step 3: 1,6-bis-(4-azidosulfonylphenoxy)-hexane (POHOP-SA)

25



A solution of 406 g sodium azide in 3.25 L water was added within
15 min to a solution of 1328 g POHOP-SC in 16.25 L acetone. The mixture
30 was stirred at room temperature for 53 h and then diluted with 14.8 L water in

order to dissolve salts. The solids were recovered by filtration and washed with 9 L water. After 2 days of drying at 40°C, 1301 g of a white solid was isolated. The chemical yield was 98% based on an assay determination of 96.6% w/w by NMR.

5 Analytical data:

 Melting point: 93 – 95°C; ¹H-NMR (300 MHz in CD₂Cl₂): 7.91 ppm (d, 4H), 7.10 ppm (d, 4H), 4.12 ppm (t, 4 H), 1.90 ppm (broad quintet, 4 H), 1.60 ppm (broad, 4 H).

10 Example 2: safety tests for POHOP-SA in comparison with DPO-BSA:

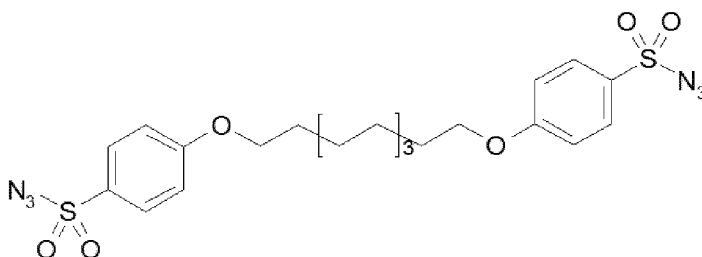
 Neat POHOP-SA is neither shock sensitive in the BAM-fallhammer test with an impact energy of 40 J, nor friction sensitive in the BAM-friction apparatus with a friction force of 360 N.

 Neat POHOP-SA is explosive according to the Koenen test with a bore
15 hole diameter of 2 mm according to the UN Manual of Tests and Criteria, Part I, Revision V, United Nations, 2009, p.33 ff (section 11.5.1).

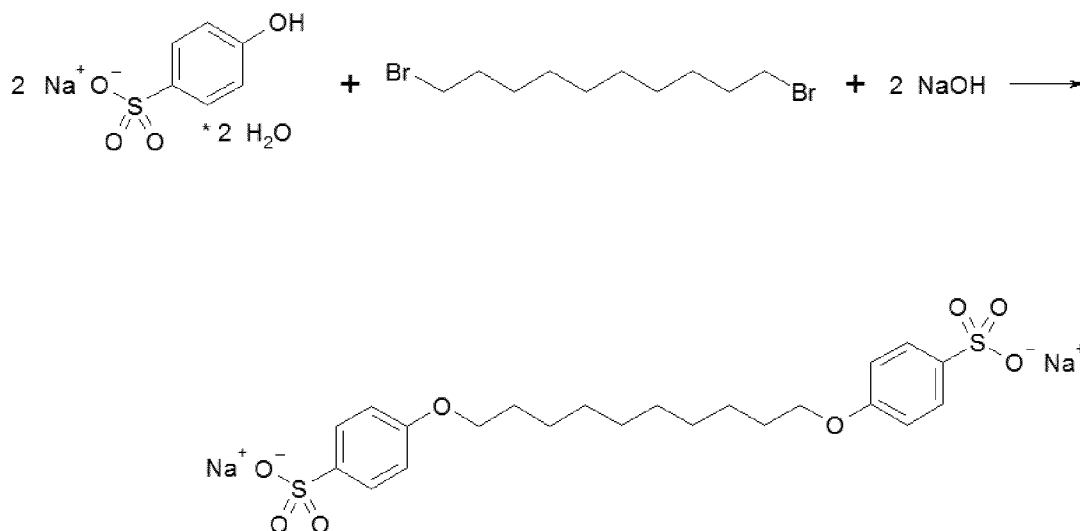
 POHOP-SA with 5 % Irganox® 1010 is still explosive in the Koenen test at 2 mm bore hole diameter but not anymore in a mixture containing 10 % Irganox® 1010.

20 For comparison, according to safety tests, POHOP-SA requires only 10% Irganox® 1010 for sufficient phlegmatization whereas the comparative example DPO-BSA requires more than 33% Irganox® 1010.

25 Example 3: synthesis of PODOP-SA



Step 1: 1,10-bis-(4-sulfophenoxy)-decane disodium salt (PODOP-SONa)

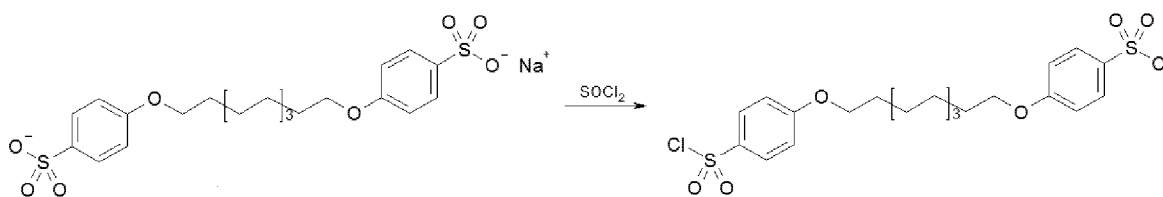


A solution of 40 g sodium hydroxide in 60 g water was added slowly at 25°C to a thin suspension of 232.2 g sodium 4-hydroxybenzene sulfonate in a mixture of 198 g water and 218 g DMSO. To this mixture, 150 g of 1,10-dibromodecane was added within 20 min. The mixture was refluxed at 113°C for 24 h, and then cooled to room temperature for filtration. The solids were washed with 0.9 L water followed by 1 L acetone and dried at 50°C. 244.6 g of a white solid with a purity of 94.1 area-% (HPLC) was isolated with a chemical yield of 87%.

Analytical data:

Melting point >350°C; ¹H-NMR (300 MHz in DMSO): 7.49 ppm (d, 4H), 6.84 ppm (d, 4H), 3.95 ppm (t, 4 H), 1.70 ppm (m, 4 H), 1.25 – 1.45 ppm (broad, 12 H).

Step 2: 1,10-bis-(4-chlorosulfonylphenoxy)-decane (PODOP-SC)



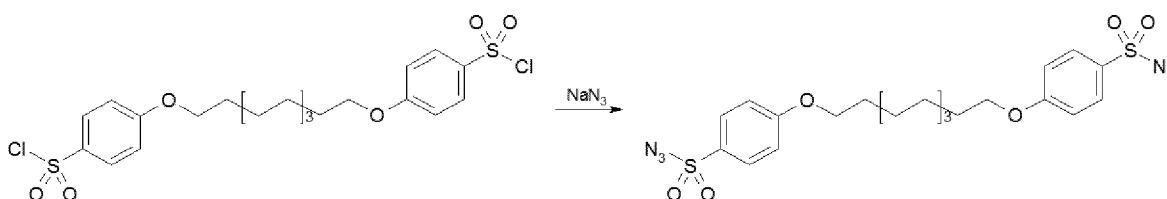
A mixture of 244.1 g PODOP-SO₃Na, 821 g thionyl chloride, and 2.4 g DMF was heated to 75°C for 7 h. 330 g thionyl chloride were removed by distillation at 50°C and 100 mbar. The residue was diluted with 900 mL petrolether 30/50 at 25°C. The solids were filtered off after 24 h and washed with 500 ml petrolether 30/50. The wet filter cake was slurried in 910 mL water

in order to remove salts and residual traces of thionyl chloride. The solids were filtered, washed with 0.5 l water, and dried at 40°C. 228.3 g of a light brown solid was obtained. The chemical yield based on the mass of the product was 98%.

5 Analytical data:

Melting point: 63 – 65°C; ¹H-NMR (300 MHz in CDCl₃): 7.98 ppm (d, 4H), 7.05 ppm (d, 4H), 4.08 ppm (t, 4 H), 1.85 ppm (broad quintet, 4 H), 1.30 – 1.60 ppm (broad, 12 H).

10 Step 3: 1,10-bis-(4-azidosulfonylphenoxy)-decane (PODOP-SA)



A solution of 69.7 g sodium azide in 609 mL water was added within 30 min to a solution of 227.7 g PODOP-SC in 3.04 L acetone. The mixture was stirred at room temperature for 24 h and then diluted with 2.53 L water in order to dissolve salts. The solids were recovered by filtration and washed with 0.6 L water. After 2 days of drying at 40°C, 210 g of a light brown solid was isolated. 208 g of the crude product was dissolved in 330 g acetone. 1 g activated charcoal and 2 g diatomaceous earth were added and the mixture was filtered at 55°C. The filtrate was cooled to 26°C when crystallization started with a temperature rise to 29°C. At this temperature, 208 mL water was added to the mixture and the solids were recovered by filtration and washed with 208 mL water. Drying at 40°C resulted in 204.7 g off-white PDOOP-SA with 98.4 area-% purity. The chemical yield was 88%.

25 Analytical data:

Melting point: 89 – 91°C; ¹H-NMR (300 MHz in DMSO): 7.93 ppm (d, 4H), 7.23 ppm (d, 4H), 4.11 ppm (t, 4 H), 1.74 ppm (broad quintet, 4 H), 1.25 – 1.45 ppm (broad, 12 H).

30

Example 4: safety tests for PODOP-SA in comparison with DPO-BSA

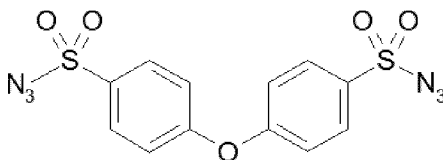
Neat PODOP-SA is neither shock sensitive in the BAM-fallhammer test with an impact energy of 40 J nor friction sensitive in the BAM-friction apparatus with a friction force of 360 N.

Neat PODOP-SA is not explosive according to the Koenen test with a bore hole diameter of 2 mm.

According to the time/pressure test, it does not deflagrate quickly.

- 5 According to these safety tests, PODOP-SA is not explosive, does not have to be included in class 1 according to transport regulations and thus does not have to be phlegmatized at all.

Comparative example: explosive properties of DPO-BSA



10

Neat DPO-BSA is shock sensitive in the BAM-fallhammer test with an impact energy of 15 J (like the commercial explosive TNT) but not friction sensitive in the BAM-friction apparatus with a friction force of 360 N.

- 15 Neat DPO-BSA is explosive according to the Koenen test with a bore hole diameter of 2 mm.

According to safety tests, DPO-BSA requires more than 33% Irganox® 1010 for sufficient phlegmatization.

20

CLAIMS

1. A compound of the general formula
- 5 (I) $\text{N}_3\text{O}_2\text{S-Ar-L-Ar}'\text{-SO}_2\text{N}_3$,
wherein:
- Ar and Ar' are aromatic building blocks; and
 - L is a linking group comprising at least one heteroatom as well
as an organic chain denoted as Sp'' and having at least two
10 carbon atoms.
2. The compound of claim 1, wherein the at least one heteroatom
in the linking group L is selected from sulfur, nitrogen, and
oxygen.
- 15 3. The compound of claim 1 or 2, wherein the organic chain Sp'' is
an aliphatic chain, and is preferably linear.
4. The compound of any one of claims 1 to 3, wherein the organic
20 chain Sp'' comprises from 2 to 20 carbon atoms, preferably from
6 to 16 carbon atoms.
5. The compound of any one of claims 1 to 4, where Ar is a phenyl
group, or Ar' is a phenyl group, and preferably Ar and Ar' are both
25 phenyl groups, said phenyl groups being substituted or not.
6. The compound of any one of claims 1 to 5, in which L is Y-Sp''-Y',
wherein:
- Y and Y' are both functional groups comprising a heteroatom,
30 which are preferably independently selected from -O-, -NH-,
-NR-, -OC(=O)NH-, -OC(=O)NR'-, -OC(=O)O-,
-NHC(=O)NH-, -NHC(=O)O-, -NHC(=O)NR'-, -NRC(=O)NH-,
-NRC(=O)O-, -NRC(=O)NR'-, -S-, -SO₂-, -C(=O)O-,

- C(=O)NH-, -C(=O)NR-, -C(=O)-, -OC(=O)-, -NHC(=O)- and -NRC(=O)-, R and R' being alkyl or aryl groups; and
- Sp'' is as defined above.

5 **7.** The compound of claim 6, in which Ar and Ar' are phenyl groups, substituted or not; L is O-Sp''-O; and the organic chain Sp'' is an aliphatic chain which preferably comprises at least 3, preferably at least 4, more preferably at least 5, and most preferably at least 6 carbon atoms.

10

8. The compound of claim 6 or 7, having the general formula:
 (I'') (N₃O₂S-Ar-Y)₂Sp'',
 wherein Ar, Y and Sp'' are as defined above.

15

9. The compound of any one of claims 1 to 8, which is the compound 1,6-bis-(4-azidosulfonylphenoxy)-hexane.

10. The compound of any one of claims 1 to 8, which is the compound 1,10-bis-(4-azidosulfonylphenoxy)-decane.

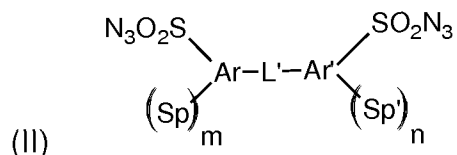
20

11. The compound of any one of claims 1 to 8, which is the compound 1,2-bis-(4-azidosulfonylphenoxy)-hexadecane.

25

12. The compound of any one of claims 1 to 8, which is an isomeric mixture of 4,8-bis-(4-azidosulfonylphenoxy)methyl)-tricyclo[5.2.1.0^{2,6}]decane.

13. A compound of the general formula



30

wherein:

- Ar and Ar' are aromatic building blocks;
- L' is a covalent bond or a linking group;

- m and n are both 0 or 1, at least one of m and n being 1;
- Sp and Sp' are organic chains having at least two carbon atoms.

5 **14.** The compound of claim 13, wherein L' comprises at least one heteroatom, preferably selected from sulfur, nitrogen, and oxygen.

10 **15.** The compound of claim 13 or 14, wherein m is 1 and n is 0; or m is 0 and n is 1.

16. The compound of any one of claims 13 to 15, wherein Sp and/or Sp' is an aliphatic chain, and is preferably linear.

15 **17.** The compound of any one of claims 13 to 16, wherein Sp and/or Sp' comprises from 2 to 20 carbon atoms, preferably from 6 to 18 carbon atoms.

20 **18.** The compound of any one of claims 13 to 17, in which L' is selected from -O-, -NH-, -NR-, -OC(=O)NH-, -OC(=O)NR'-, -OC(=O)O-, -NHC(=O)NH-, -NHC(=O)O-, -NHC(=O)NR'-, -NRC(=O)NH-, -NRC(=O)O-, -NRC(=O)NR'-, -S-, -SO₂-, -C(=O)O-, -C(=O)NH-, -C(=O)NR-, -C(=O)-, -OC(=O)-, -NHC(=O)- and -NRC(=O)-, R and R' being alkyl or aryl groups.

25 **19.** The compound of any one of claims 13 to 18, in which L' is -O-, Ar and Ar' are phenyl groups, and Sp and/or Sp' is an aliphatic chain comprising at least 3, preferably at least 4, more preferably at least 5 and most preferably at least 6 carbon atoms.

30 **20.** The compound of any one of claims 13 to 19, which is the compound 4,4'-bis-(azidosulfonyl)-3-pentadecyl diphenylether.

21. The compound of any one of claims 13 to 19, which is 4,4'-bis-(azidosulfonyl)-2-hexadecyl diphenylether and/or 4,4'-bis-(azidosulfonyl)-2-octadecyl diphenylether.
- 5 22. The compound of any one of claims 13 to 19, which is 1,6-bis-(4-azidosulfonyl-3-pentadecylphenoxy)hexane.
- 10 23. A process for producing the compound according to any one of claims 1 to 22, which comprises providing starting compounds A and B, wherein A and B are substituted aromatic compounds, and which comprises a step of reacting A and B.
- 15 24. The process of claim 23, for producing a compound according to one of claims 1 to 12, wherein the starting compounds A and B are reacted in the presence of an additional compound Z-Sp''-Z', Sp'' being the organic chain defined above, and Z and Z' being two reactive groups ; and wherein A and B are preferably identical.
- 20 25. The process of claim 23, for producing a compound according to one of claims 13 to 22, wherein the step of reacting A and B is followed by a step of chlorosulfonating the obtained product, and then a step of reacting the obtained product with sodium azide.
- 25 26. A composition comprising the compound according to any one of claims 1 to 22, and containing at most 50% (w/w), preferably at most 40% (w/w), more preferably at most 30% (w/w), even more preferably at most 20% (w/w), most preferably at most 10% (w/w) of a phlegmatizing agent.
- 30 27. The use of the compound according to any one of claims 1 to 22, as a crosslinker.

- 5 **28.** The use according to claim 27, wherein said compound is used with at most 50% (w/w), preferably at most 40% (w/w), more preferably at most 30% (w/w), even more preferably at most 20% (w/w), most preferably at most 10% (w/w) of a phlegmatizing agent.
- 29.** The use according to claim 27, wherein said compound is used without any phlegmatizing agent.
- 10 **30.** The use according to any one of claims 27 to 29, as a crosslinker in the manufacture of polyolefins, polyolefin copolymers and blends of polyolefins, preferably in the manufacture of polypropylene or polyethylene.
- 15 **31.** The use according to any one of claims 27 to 29, as a crosslinker in the manufacture of elastomers, elastomer copolymers and blends of elastomers, preferably in the manufacture of EPM, EPDM and EPM-polyolefin blends.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/055345

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C381/00 C08J9/00 C08B5/08
ADD.

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)
C07C C08J C08B

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 practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/178243 A1 (J.W. MCMICHAEL, ET AL.) 21 July 2011 (2011-07-21)	1-8, 13-19, 26-31
Y	paragraphs [0005], [0052] -----	23-25
A	US 3 298 975 A (FEILD GEORGE B ET AL) 17 January 1967 (1967-01-17) cited in the application column 2, lines 27-58; claim 1 -----	1-31
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Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/055345

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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