

Antifouling Composition

Field of the Invention

5 The present invention relates to marine antifouling coating compositions, more specifically to marine antifouling coating compositions comprising a particular binder and to the binder itself. The invention further relates to kits suitable for the preparation of the antifouling coating compositions and to surfaces coated with the antifouling coating compositions.

Background

10 Surfaces that are submerged in seawater are subjected to fouling by marine organisms such as green and brown algae, barnacles, mussels, tube worms and the like. On marine constructions such as vessels, oil platforms, buoys, etc. such fouling is 15 undesired and has economical consequences. The fouling may lead to biological degradation of the surface, increased load and accelerated corrosion. On vessels the fouling will increase the frictional resistance which will cause reduced speed and/or increased fuel consumption. It can also result in reduced manoeuvrability.

20 Also underwater structures, e.g. industrial plant, pipes and tanks for fresh water storage that are exposed to an aqueous environment, like rivers, lakes, canals and swimming pools, have the similar problem caused by the attachment and growth of living organisms. This causes severe economic losses because of decreased possible operation time.

25 To prevent settlement and growth of marine organisms antifouling paints are used. These paints generally comprise a film-forming binder, together with different components such as pigments, fillers, solvents and biologically active substances.

30 The most successful antifouling coating system on the market until 2003 was a tributyltin (TBT) self-polishing copolymer system. The binder system for these antifouling coatings was a linear acrylic copolymer with tributyltin pendant groups. In seawater the polymer was gradually hydrolysed releasing tributyltin, which is an effective biocide. The remaining acrylic copolymer, now containing carboxylic acid

groups, became sufficiently soluble or dispersible in seawater to be washed out or eroded away from the coating surface. This self-polishing effect provided a controlled release of the biologically active compounds in the coating resulting in excellent antifouling efficiency and smooth surfaces and hence reduced frictional resistance.

5 The IMO Convention "International Convention on the Control of Harmful Anti-fouling Systems on Ships" of 2001 prohibited the application of new TBT containing antifouling coatings from 2003 and TBT containing antifouling coatings are prohibited on ship hulls from 2008.

10 In recent years new antifouling coating systems have been developed and introduced as a consequence of the TBT ban. One broad group of biocidal antifouling coatings on the market today is the self-polishing antifouling coatings which mimic the TBT self-polishing copolymer coatings. Those antifouling coatings are based on (meth)acrylic copolymers having pendant hydrolysable groups without biocidal properties. The hydrolysis mechanism is the same as in the TBT containing
15 copolymers. This gives the same controlled dissolution of the polymers and thereby the controlled release of antifouling compounds from the coating film, resulting in similar performance as the TBT containing antifouling coating systems. The most successful self-polishing antifouling systems today are based on silyl ester functional (meth)acrylic copolymers. These coating compositions are for example described in, EP
20 0 646 630, EP 0 802 243, EP 1 342 756, EP 1 479 737, EP 1 641 862, WO 00/77102, WO 03/070832 and WO 03/080747. The hydrolysable binder provides a continuous renewal of the coating film and efficient release of biocides at the coating surface, and thereby keeping the surface free of organisms.

25 The above mentioned antifouling coating systems degrade by hydrolysis of pendant groups on the polymer backbone, which results in a water erodable polymer. The hydrolysis of the pendant groups on the polymer backbone results in the formation of carboxylic acid salts which make the polymer hydrophilic and thereby erodable. A certain amount of hydrolysable groups are needed to get sufficient hydrophilicity and an erodable polymer after hydrolysis.

30 Another way of obtaining water erodable polymers is by introducing hydrolysable groups in the polymer backbone, resulting in degradation of the polymer structure, which gives erosion of the polymer film or coating film. Polyhydrides are a

class of polymers that degrade by backbone hydrolysis. The polyanhydrides are well documented for their surface degradation properties. Surface degradation is one of the most important factors for obtaining a successful antifouling coating. The use of specific aromatic polyanhydrides as binders in antifouling coating compositions is, for example, described in WO 2004/096927.

However, the anhydride group is extremely labile in the presence of moisture and it is therefore difficult to design a coating system based on polyanhydrides that exhibits a slow, controlled hydrolysis for use in antifouling coatings. Accordingly, the polyanhydrides used for antifouling coating compositions generally have a high content of aromatic units in order to control the hydrolysis.

In recent years, polyoxalates have emerged as a class of polymers that are well suited for use as binders in antifouling coatings. Backbone hydrolysis in these compounds is more controlled than for the polyanhydrides.

The use of self-polishing binders in which the polymer backbone hydrolyses in sea water makes it possible to obtain erodable cross-linked polymers and high molecular weight polymers.

An alternative to the anti-fouling coatings (which necessarily contain a biocide), are the so called fouling release coatings. These coatings have low surface tension and low modulus of elasticity and work by providing a “non-stick” surface to which sea organisms cannot stick or if they can stick are washed off by the motion of the water against the surface. Coatings are often based on polysiloxane/silicone/polydimethylsiloxane (PDMS) that generally have very low toxicity. There are disadvantages of the fouling release system. For example, when applied to boat hulls the accumulation of marine organisms is reduced but relatively high vessel speeds are needed to remove all fouling species. Thus, in some instances, it has been shown that for effective release from a hull that has been treated with such a polymer, it is necessary to sail with a speed of at least 14 knots.

Such “non-stick” coatings have however, not shown good resistance to soft fouling such as slime and algae over time. Adding biocides in combination with a hydrophilic modified PDMS oil to such PDMS coatings has been suggested to overcome this problem in WO2011/076856. WO2013/00479 relies on the same

principles of addition of biocides, but here hydrophilic modified polysiloxane moieties are covalently bonded to the polysiloxane binder.

These mixed materials have found limited commercial success however, as diffusion of biocides to the surface is too fast at the start of the coating lifetime, and then diffusion stops as the coating ages. More recently, Azemar, in Progress in Organic coatings 87, 2015, 10-19 discusses hybrid coatings based on a triblock copolymer of polycaprolactone and PDMS. A PDMS block is co-polymerized with caprolactone to obtain polycaprolactone polymer blocks on each end of a PDMS block. The polymers therefore contain only one PDMS block with two polyester blocks formed from the caprolactone meaning that any hydrolysis occurs only at the end of the molecule and not in the centre of any chain. Poly(caprolactone units) cannot be used in the manufacture of a copolymer as we claim as it does not contain two identical functional groups.

In WO2004/085560 polysilylestere are disclosed formed by the reaction of a dicarboxylic acid and an acyloxysilyl compound. The resulting polymer is suggested for use as a binder in anti-fouling coatings. The claimed polymer always contains a characteristic silyl-ester Si-O-CO- link in the backbone however. Silyl-esters are known to be very reactive towards moisture with complete degradation occurring within days or weeks. The compounds in '560 are much too labile to be used successfully in long term anti-fouling coating compositions which need to be in service for years. We also observe that the process for the manufacture of these silyl ester polymers is complex. Our solution uses a much simpler process and avoids problems associated with distillation of acids, for example.

In WO2015/082397, a coating composition is taught which contains a binder formed from the reaction of a polysiloxane and a lactone. This gives rise to a polymer chain containing a -CO-alkylene-O- group. This is achieved via the ring opening of a lactone. Moreover, this polymerisation results in a block copolymer as the ring opened lactone can react with other lactones to extend the polymerisation. The polymer is therefore a triblock polymer of structure AAABBBAAA. In order to obtain a curable polymer relatively high organic-to-siloxane ratios are necessary. This process leads to polymers which have much higher glass transitions compared to conventional

polysiloxanes. This limits the non-stick character, softness and release potential of the polymers.

There remain problems to be solved, in particular, with regard to fouling release coating performance over time.

5 The present inventors have appreciated that it would be beneficial to have a fouling release coating surface that is renewable. The use of a renewable surface means that slime/algae and other soft fouling are physically removed with or without the need for biocides. It would therefore be useful if the fouling release coating composition could offer a renewable surface like that of an anti-fouling coating composition. This
10 can be achieved with or without the addition of biocides. Biocides might be employed for example where a substrate, such as a ship's hull might be exposed to low speed or heavy fouling conditions.

 The object of the present invention is to provide a new binder for a coating composition that can prevent marine organisms, both animals such as barnacles and
15 algae/slime, adhering to the surface of underwater structures such as ship hulls. The idea of the invention is to combine the benefits of the fouling release type coating and the self-polishing anti-fouling coating, to provide, *inter alia*, a renewable non-stick surface on a substrate. The binder may or may not be provided with a biocide to potentially prolong the anti-fouling effect of the coating.

20 The invention therefore combines the benefits of the two technologies to provide a renewable coating with low surface tension optionally with biocides.

 The invention achieves this aim using a copolymer made by polymerising polysiloxane units with shorter comonomer molecules which are not polysiloxanes to provide a polymer containing hydrolysable ester units in its backbone. The binder is
25 formed via the copolymerisation of a monomer unit comprising a thiol group with a monomer unit comprising a vinyl group or thiol with which that thiol group can react. Alternatively, the binder is formed via the copolymerisation of a monomer unit comprising an amine group with a monomer unit comprising a vinyl group with which that amine group can react.

30 The inventors have surprisingly found that the polymers designed herein are able to hydrolyse in sea water to renew the surface and, if desired allow leaching of any

biocide within the coating. Also, the binders of the invention provide a coating composition that has low VOC, low surface energy and low modulus of elasticity.

Summary

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Thus, disclosed is a binder for a coating composition especially a marine coating composition, wherein said binder comprises a polymer comprising a polysiloxane group, a plurality of ester groups, and a plurality of thio groups (e.g. of formula $-(C-S-CH_2)-$, such as $-(CH_2-S-CH_2)-$, amino groups or disulphide groups S-S.

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Disclosed is a binder for a coating composition, wherein said binder comprises a polymer comprising in its backbone a polysiloxane group, a plurality of ester groups, and a plurality of thio, amino or disulphide groups.

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In particular, the disclosure provides a binder for a coating composition, wherein said binder comprises a polymer comprising in its backbone a plurality of polydimethylsiloxane groups, a plurality of ester groups, and a plurality of thio groups (e.g. of formula $-(C-S-CH_2)-$, such as $-(CH_2-S-CH_2)-$, amino groups (e.g. of formula $CH_2-NR_a-CH_2-$) or S-S (where R_a is H or C1-6 alkyl).

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In particular, the disclosure provides a binder for a coating composition, wherein said binder comprises a polymer comprising in its backbone a repeating unit which comprises a plurality of polydimethylsiloxane groups, a plurality of ester groups, and a plurality of thio groups (such as those of formula $-(CH_2-S-CH_2)-$), amino or S-S groups.

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Disclosed is a binder for a coating composition comprising the reaction product of a vinyl terminated polysiloxane polyester monomer and a bis-thiol monomer or bisamino monomer.

Disclosed is a binder for a coating composition comprising the reaction product of a thiol terminated polysiloxane monomer and a vinyl terminated polyester monomer.

Disclosed is a binder for a coating composition comprising the reaction product of a vinyl terminated polysiloxane monomer and a thiol terminated polyester monomer.

30

Disclosed is a binder for a coating composition comprising the reaction product of a vinyl terminated polysiloxane polyester monomer and a thiol terminated polyester monomer or amino terminated polyester monomer.

5 Disclosed is a binder for a coating composition comprising the reaction product of a thiol terminated polysiloxane monomer and a thiol terminated polyester monomer.

Disclosed is a binder for a coating composition comprising the reaction product of a thiol terminated polysiloxane polyester monomer and a thiol terminated monomer.

10 Disclosed is a binder for a coating composition comprising the reaction product of a thiol terminated polysiloxane polyester monomer and a thiol terminated polyester monomer.

Disclosed is a binder for a coating composition comprising the reaction product of an amino terminated polysiloxane monomer and a vinyl terminated polyester monomer.

In any of the monomers above, said polyester is preferably a diester.

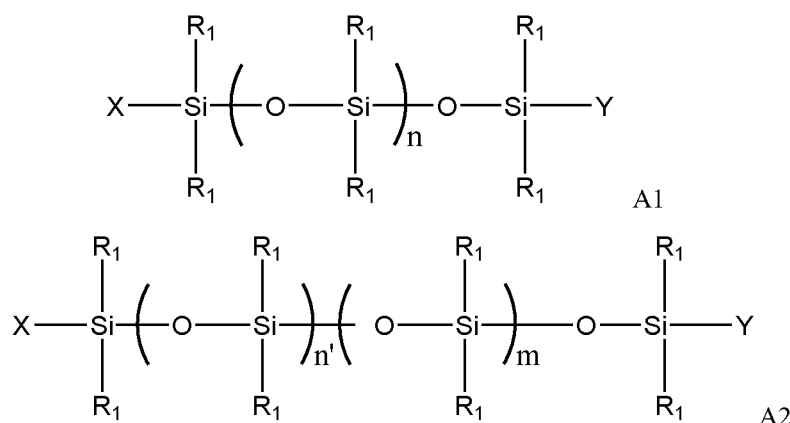
15 In an especially preferred embodiment, the polymer is the reaction product of a (meth)acryloxyalkyl terminated polysiloxane monomer and a bithiol monomer, such as a thiol terminated polyester monomer, or bisamino monomer.

In an especially preferred embodiment, the polymer is the reaction product of a thiol functionalised polysiloxane monomer and a vinyl terminated polyester monomer.

20 In an especially preferred embodiment, the polymer is the reaction product of a vinyl terminated polysiloxane monomer and a thiol terminated polyester monomer.

In an especially preferred embodiment, the polymer is the reaction product of a thiol functionalised polysiloxane monomer and a thiol terminated polyester polyol monomer.

25 Disclosed is a binder for a coating composition, such as a marine coating composition, comprising the reaction product of at least one polysiloxane monomer A' of general formula (A1) or (A2):



wherein each R_1 is the same or different and represents an unsubstituted or
 5 substituted C_{1-20} alkyl, C_{2-20} alkenyl, C_{3-20} cycloalkyl, C_{6-20} aryl, C_{7-20} arylalkyl group,
 or a polyoxyalkylene chain, especially methyl;

X and Y can be the same or different and represent $-\text{CR}=\text{CH}_2$; $-(\text{CR}'')_x-$
 $\text{CR}=\text{CH}_2$; $-(\text{CR}'')_x-\text{CR}''_2-\text{OCO}-\text{CR}=\text{CH}_2$; $-\text{CR}''_2-\text{OCO}-\text{CR}=\text{CH}_2$; $-(\text{CR}'')_x-\text{SH}$; -
 $(\text{CR}'')_x-\text{O}-(\text{CR}'')_x-\text{SH}$; $-(\text{CR}'')_x-[\text{O}-(\text{CR}'')_x]_f-\text{OCO}-\text{CR}=\text{CH}_2$; $-(\text{CR}'')_x-(\text{OR}^8)_a-$
 10 $(\text{OR}^8)_b-\text{OR}^7-\text{SH}$; $-(\text{CR}'')_x-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7-\text{CR}=\text{CH}_2$; $-\text{CR}''_2-\text{Ar}-\text{CR}''_2-\text{SH}$; -
 $(\text{CR}'')_x-\text{C}\equiv\text{CH}$; $-(\text{CR}'')_x-\text{O}-(\text{CR}'')_x-(\text{CHOH})-(\text{CR}'')_x-\text{OCO}-\text{CR}=\text{CH}_2$; or $-(\text{CR}'')_x-$
 $(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7-\text{C}\equiv\text{CH}$;

R'' is independently C_{1-6} alkyl or H, especially H;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

15 each R is independently H or Me;

where R^7 and R^8 are each independently C_{2-6} alkylene and $a=0-50$, $b=0-50$ and
 $a+b=1-50$;

f is 1 to 50;

Ar is C_6-12 aryl; and

20 n is 1-500, more preferably 10-300, especially 15-100;

or $n' + m$ add to 1-500, more preferably 10-300, especially 15-100;

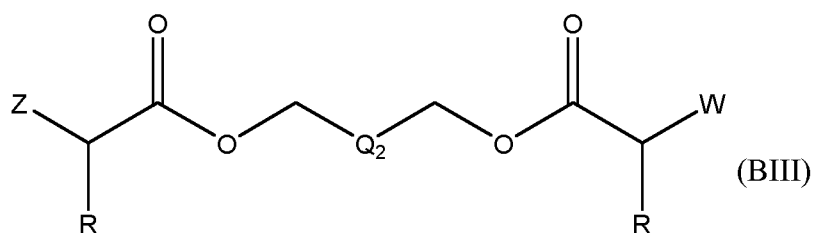
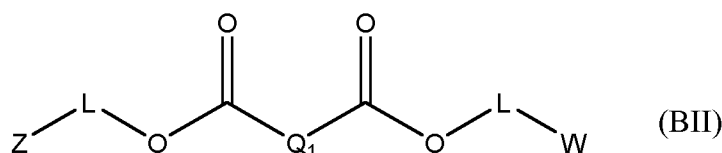
and at least one second monomer B' of formula BI

HS-Q3-SH (BI)

wherein Q3 is C2-20 alkyl, C3-20 cycloalkyl, phenyl, biphenyl, terphenyl, C7-20 alkylaryl group, alkyl-polysiloxane-alkyl, C4-20 alkylcycloalkyl or polyether;

wherein said C2-20 alkyl, C3-20 cycloalkyl, C7-20 alkylaryl group, or C4-20 alkylcycloalkyl optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

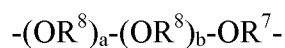
with the proviso that the SH groups in monomer B' react with the X and Y groups in ester containing monomer A' to form a group C-S-CH₂ or S-S group; or at least one second monomer B' of formula (BII) or (BIII)



wherein Q1 represents covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, a polyoxyalkylene chain of formula R⁷-(OR⁸)_a-(OR⁸)_b-OR⁷, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C4-10 alkylcycloalkyl;

wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

L is C1-20 alkylene optionally comprising one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O or N, or a polyoxyalkylene chain of formula:



where R^7 and R^8 are each independently C_{2-6} alkylene and $a=0-50$, $b=0-50$ and $a+b=1-50$;

R is H or Me;

Q2 is a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

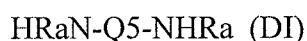
W and Z are each $-SH$, $-(CR''_2)_x-SH$, $CH_2=CR-$; $CH_2=CR-(CR''_2)_x-$, $-C\equiv CH$, $-NHCH_2-CR=CH_2$, $NHCH_2-CR\equiv CH-NHRa$, $-NHRa$ or W and Z are $=CH_2$ (thus forming a double bond with the C atom to which W/Z is attached);

Ra is H or C1-6 alkyl wherein said alkyl group optionally comprises one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

R'' is independently C_{1-6} alkyl or H, especially H;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

with the proviso that the W and Z groups in monomer B' react with the X and Y groups monomer A' to form a group C-S-CH₂, an amino group or S-S group; or at least one second monomer D' of formula:



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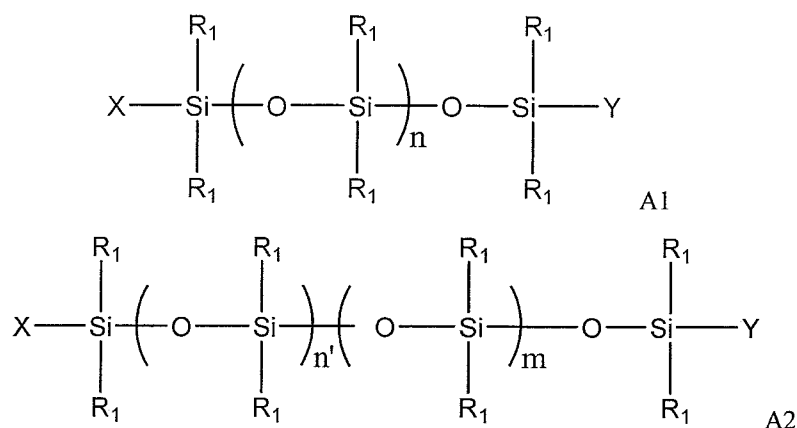
wherein Q5 is C2-20 alkyl, C2-20 alkenyl, C3-20 cycloalkyl, phenyl, biphenyl, terphenyl, Ph-O-Ph, C7-20 alkylaryl group, alkyl-polysiloxane-alkyl, C4-20 alkylcycloalkyl, C3-10 heterocyclic group or polyether (such as a $-(CH_2)_3O-(CH_2CH_2O)_r(CH(CH_3)CH_2O)_s(CH_2)_3-$ where $r+s$ is 1 to 100) wherein said C2-20 alkyl, C3-20 cycloalkyl, C7-20 alkylaryl group, or C4-20 alkylcycloalkyl optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

Ra is H or C1-6 alkyl;

with the proviso that the N Ra H groups in monomer D' react with X and Y groups in ester containing monomer A' to form a group C-N Ra -CH₂.

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In one aspect, there is provided a binder for a coating composition comprising the reaction product of at least one polysiloxane monomer A' of general formula (A1)-(A2):



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wherein each R_1 is the same or different and represents an unsubstituted or substituted C_{1-20} alkyl, C_{2-20} alkenyl, C_{3-20} cycloalkyl, C_{6-20} aryl, C_{7-20} arylalkyl group, or a polyoxyalkylene chain;

X and Y can be the same or different and represent $-\text{CR}=\text{CH}_2$, $-(\text{CR}'')_{x'}$, $-\text{CR}=\text{CH}_2$, $-(\text{CR}'')_{x'}-\text{CR}''_2-\text{OCO}-\text{CR}=\text{CH}_2$, $-\text{CR}''_2-\text{OCO}-\text{CR}=\text{CH}_2$, $-(\text{CR}'')_{x'}-\text{SH}$; $-(\text{CR}'')_{x'}-\text{O}-(\text{CR}'')_{x'}-\text{SH}$, $-(\text{CR}'')_{x'}[\text{O}-(\text{CR}'')_{x'}]_f-\text{OCO}-\text{CR}=\text{CH}_2$, $-(\text{CR}'')_{x'}-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7-\text{SH}$, $-(\text{CR}'')_{x'}-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7-\text{CR}=\text{CH}_2$, $-\text{CR}''_2-\text{Ar}-\text{CR}''_2-\text{SH}$, $-(\text{CR}'')_{x'}\text{C}\equiv\text{CH}$, $-(\text{CR}'')_{x'}-\text{O}-(\text{CR}'')_{x'}-(\text{CHOH})-(\text{CR}'')_{x'}-\text{OCO}-\text{CR}=\text{CH}_2$ or $-(\text{CR}'')_{x'}-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7\text{C}\equiv\text{CH}$;

15 R'' is independently C_{1-6} alkyl or H, especially H;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

each R is independently H or Me;

where R^7 and R^8 are each independently C_{2-6} alkylene and $a=0-50$, $b=0-50$ and $a+b=1-50$;

20 f is 1 to 50;

Ar is C_6-12 aryl; and

n is 1-500, more preferably 10-300, especially 15-100;

or $n' + m$ add to 1-500, more preferably 10-300, especially 15-100;

and at least one second monomer B' of formula

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HS-Q3-SH (BI)

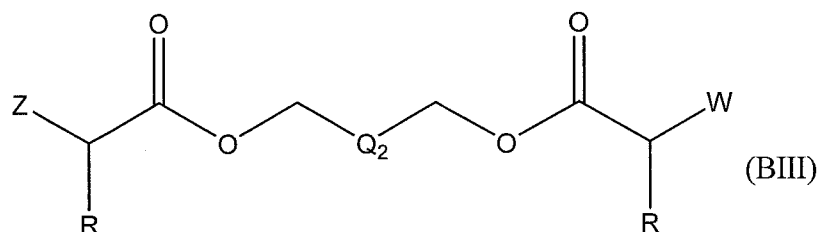
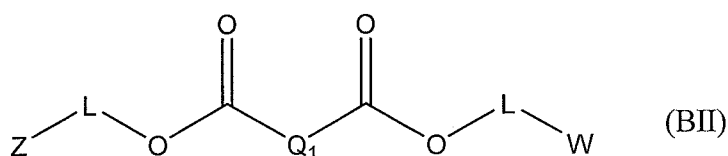
wherein Q3 is C2-20 alkyl, C3-20 cycloalkyl, phenyl, biphenyl, terphenyl, C7-20 alkylaryl group, alkyl-polysiloxane-alkyl, C4-20 alkylcycloalkyl or polyether;

wherein said C2-20 alkyl, C3-20 cycloalkyl, C7-20 alkylaryl group, or C4-20 alkylcycloalkyl optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

with the proviso that the SH groups in monomer B' react with the X and Y groups in ester containing monomer A' to form a group C-S-CH₂ or S-S group; or

at least one second monomer B' of formula (BII) or (BIII)

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wherein Q1 represents a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, a polyoxyalkylene chain of formula R⁷-(OR⁸)_a-(OR⁸)_b-OR⁷, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C4-10 alkylcycloalkyl; wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

L is C1-20 alkylene optionally comprising one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O or N, or a polyoxyalkylene chain of formula:



where R^7 and R^8 are each independently C_{2-6} alkylene and $a = 0-50$, $b = 0-50$ and $a+b = 1-50$;

R is H or Me;

Q2 is a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

W and Z are $-SH$, $-(CR''_2)_xSH$, $CH_2=CR-$, $CH_2=CR-(CR''_2)_x-$, $-C\equiv CH$, $-NHCH_2-CR=CH_2$, $NHCH_2-CR\equiv CH-NHRa$, $-NHRa$ or W and Z are $=CH_2$ (thus forming a double bond with the C atom to which W/Z is attached);

Ra is H or C1-6 alkyl wherein said alkyl group optionally comprises one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

R'' is independently C_{1-6} alkyl or H, especially H;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

Ra is H or C1-6 alkyl wherein said alkyl group optionally comprises one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

with the proviso that the W and Z groups in monomer B' react with the X and Y groups monomer A' to form a group $C-S-CH_2$, an amino group or S-S group;

or at least one second monomer D' of formula:

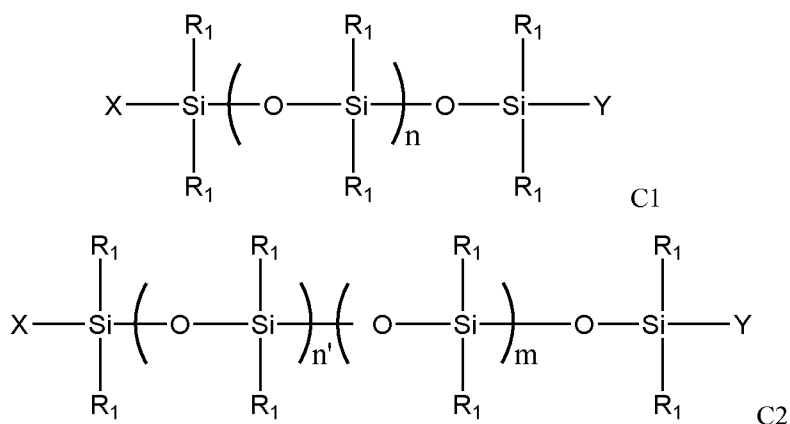
$H Ra N-Q5-N H Ra$ (DI)

wherein Q5 is C2-20 alkyl, C2-20 alkenyl, C3-20 cycloalkyl, phenyl, biphenyl, terphenyl, Ph-O-Ph, C7-20 alkylaryl group, alkyl-polysiloxane-alkyl, C4-20 alkylcycloalkyl, C3-10 heterocyclic group or polyether (such as a $-(CH_2)_3O-(CH_2CH_2O)_r(CH(CH_3)CH_2O)_s(CH_2)_3-$ where $r+s$ is 1 to 100) wherein said C2-20 alkyl, C3-20 cycloalkyl, C7-20 alkylaryl group, or C4-20 alkylcycloalkyl optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

Ra is H or C1-6 alkyl;

with the proviso that the $N Ra H$ groups in monomer D' react with X and Y groups in ester containing monomer A' to form a group $C-N Ra-CH_2$.

Disclosed is a binder for a coating composition comprising the reaction product of at least one polysiloxane monomer C' of general formula (C1)-(C2):



5 wherein each R₁ is the same or different and represents an unsubstituted or substituted C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₃₋₂₀ cycloalkyl, C₆₋₂₀ aryl, C₇₋₂₀ arylalkyl group, or a polyoxyalkylene chain;

X and Y can be the same or different and represent -(CR''₂)_x-NRaH, -(CR''₂)_x-NH-(CR''₂)_x-NRaH, , -(CR''₂)_x-O-(C1-6 alkyl)_x-NRaH, -(CR''₂)_x-(O-C2-6 alkyl)_x-NRaH, -(CR''₂)_x-O-(CR''₂)_x-NRaH, or -CR''₂-Ar-CR''₂-NRaH;

R'' is independently C₁₋₆ alkyl or H, especially H;

Ra is H or C1-6 alkyl;

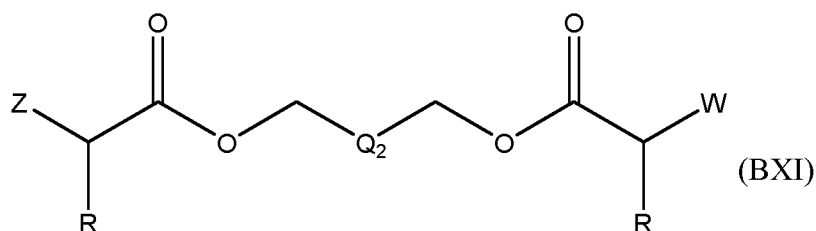
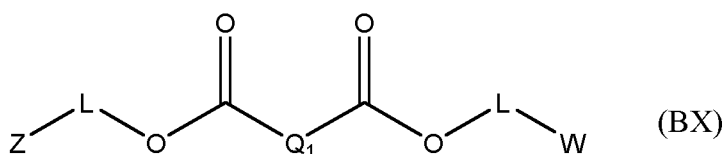
x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

and

15 n is 1-500, more preferably 10-300, especially 15-100;

or n' + m add to 1-500, more preferably 10-300, especially 15-100; and

at least one second monomer B' of formula (BX) or (BXI)



wherein Q1 represents a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, a polyoxyalkylene chain of formula $\text{R}^7-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7$, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C4-10 alkylcycloalkyl;
 5 wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

L is C1-20 alkylene, or a polyoxyalkylene chain of formula:

10



where R^7 and R^8 are each independently C₂₋₆ alkylene and $a=0-50$, $b=0-50$ and $a+b=1-50$;

15

R is H or Me;

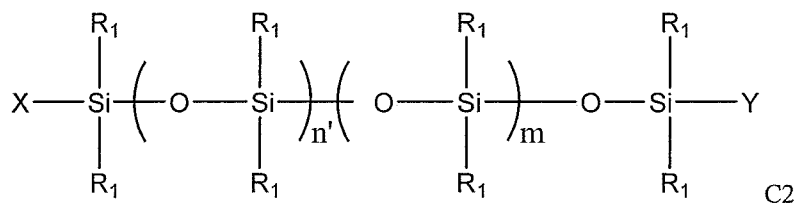
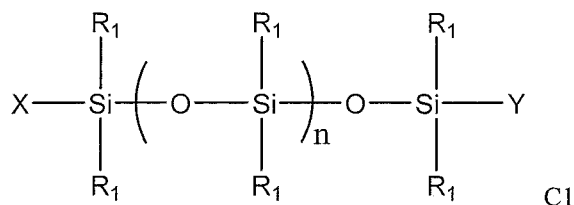
Q2 is a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl wherein said C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

20

W and Z are $\text{CH}_2=\text{CR}-$; $\text{CH}_2=\text{CR}-\text{CH}_2-$, $-\text{C}\equiv\text{CH}$, or W and Z are $=\text{CH}_2$ (thus forming a double bond with the C atom to which W/Z is attached);

with the proviso that the W and Z groups in monomer B' react with the amino X and Y groups in monomer C' to form a group $\text{C}-\text{NRa}-\text{CH}_2-$.

In another aspect, there is provided a binder for a coating composition comprising the reaction product of at least one polysiloxane monomer C' of general formula (C1)-(C2):



5

wherein each R₁ is the same or different and represents an unsubstituted or substituted C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₃₋₂₀ cycloalkyl, C₆₋₂₀ aryl, C₇₋₂₀ arylalkyl group, or a polyoxyalkylene chain;

10

X and Y can be the same or different and represent -(CR''₂)_x-NRaH, -(CR''₂)_x-NH-(CR''₂)_x-NRaH, -(CR''₂)_x-(O-C2-6 alkyl)_x-NRaH, -(CR''₂)_x-O-(CR''₂)_x-NRaH, or -CR''₂-Ar-CR''₂-NRaH;

R'' is independently C₁₋₆ alkyl or H, especially H;

Ra is H or C₁₋₆ alkyl;

15

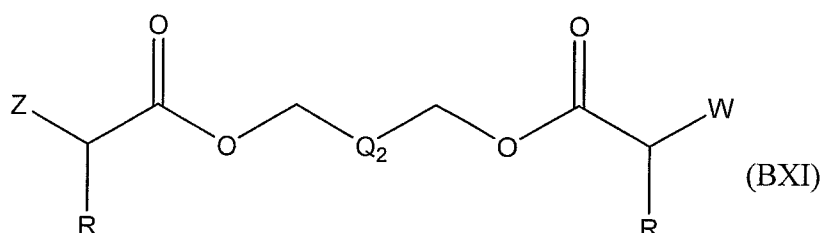
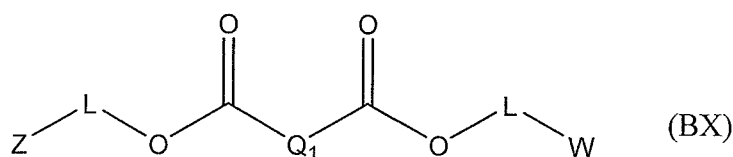
x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

and

n is 1-500, more preferably 10-300, especially 15-100;

or n' + m add to 1-500, more preferably 10-300, especially 15-100; and

at least one second monomer B' of formula (BX) or (BXI)



wherein Q₁ represents a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, a polyoxyalkylene chain of formula R⁷-(OR⁸)_a-(OR⁸)_b-OR⁷, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C4-10 alkylcycloalkyl;
 5 wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

L is C1-20 alkylene optionally comprising one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O or N, or a polyoxyalkylene chain
 10 of formula:



where R⁷ and R⁸ are each independently C₂₋₆ alkylene and a= 0-50, b= 0-50 and a+b = 1-50;

R is H or Me;

15 Q₂ is a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl wherein said C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

20 W and Z are CH₂=CR-; CH₂=CR-CH₂-, NHCH₂-CR=CH₂, -C≡CH, or W and Z are =CH₂ (thus forming a double bond with the C atom to which W/Z is attached);

with the proviso that the W and Z groups in monomer B' react with the amino X and Y groups in monomer C' to form a group C-NRa-CH₂.

Disclosed is a fouling release coating composition comprising a binder as hereinbefore defined and at least one of filler, pigment, solvent, additive, curing agent and catalyst, preferably in the absence of a biocide.

5 In another aspect, there is provided a fouling release coating composition comprising a binder and at least one additive oil, preferably in the absence of a biocide; or

an anti-fouling coating composition comprising a binder and at least one marine anti-fouling agent,

10 wherein said binder comprises a polymer comprising a polysiloxane group, a plurality of ester groups, and a plurality of thio groups, amino groups or disulphide groups.

Disclosed is an anti-fouling coating composition comprising a binder as hereinbefore defined and at least one anti-fouling agent.

15 In another aspect, there is provided a fouling release coating composition comprising a binder as described herein and at least one of filler, pigment, solvent, additive, curing agent and catalyst, preferably in the absence of a biocide;

or an anti-fouling coating composition comprising a binder as described herein and at least one anti-fouling agent.

20 In another aspect, there is provided a process for protecting an object from fouling comprising coating at least a part of said object which is subject to fouling with a coating composition as hereinbefore described and preferably curing the composition.

In another aspect, there is provided an object coated with a coating composition as hereinbefore defined, preferably a cured composition.

25 Disclosed is a process for the preparation of a binder for a marine coating composition comprising copolymerising a polysiloxane unit A' and at least one second monomer B' as herein defined so as to form an -ABAB- copolymer in which hydrolysable ester functional groups are present in the backbone of the copolymer.

Disclosed is use of a binder as hereinbefore defined for use in a fouling release composition or a marine anti-fouling coating composition.

Definitions

5 The terms biocide and anti-fouling agent are used interchangeably herein and are defined below.

 The nomenclature (meth) implies the optional presence of the methyl group.

 The binder of the invention contains multiple ester hydrolysable groups in the backbone of the molecule. The ester hydrolysable functional group is a group that
10 undergoes hydrolysis in seawater. The polymer should preferably contain a plurality of

hydrolysable ester groups in the backbone of the polymer, such as 3 or more. Other hydrolysable groups might also be present.

It will be understood that the hydrolysis reaction is one whose rate is highly dependent on both the chemical structure/composition of a compound/binder as well as the surrounding environmental conditions (salinity, pH, temperature, moisture content, etc.). The hydrolysable group should be one which hydrolyses at a temperature of 0-35°C, and at a pH and salinity reflective of natural sea water.

The ester “hydrolysable group” should be one that undergoes a hydrolysis reaction at a rate sufficient as to cause a coating surface polishing effect when said surface is moving through sea water, i.e. undergo hydrolysis in sea water at a temperature range of 0-35°C, and at a pH and salinity reflective of natural sea water.

For the avoidance of doubt, ethers, thioethers, amides and amines are not considered hydrolysable. The siloxane group is not considered hydrolysable.

Ester hydrolysable groups need to be present in the backbone of the polymer. The ester hydrolysable groups repeat in the backbone. Whilst there may be hydrolysable groups in side chains of the polymer, hydrolysable groups must be present in the backbone of the polymer.

In order to be effective, the ester hydrolysable groups should be spread throughout the polymer molecule, rather than located only at the ends of the molecule for example. The copolymer of the invention is preferably not a block copolymer in which there are blocks of polysiloxane and end blocks of another material such as a polyester, i.e. a polymer of structure AAAABBBBBBAAAA. Rather, the copolymer of the invention is preferably of structure $-[ABAB]-$, with at least two repeating units of monomer A' (or C') and at least two repeating units of monomer B' (or D' etc). It will be appreciated that there can be many repeating units and the formula $-[ABAB]-$ is intended to encompass copolymers with any number of AB repeating units. We define molecular weights below.

The monomers A' and B' (or A' and D' or C' and B' etc) react together to form polymer repeating units A and B (or AD etc).. Typically, the linker group that forms is a thio linker of formula $-(C-S-CH_2)-$ such as $-(CH_2-S-CH_2)-$. A thio group in the backbone of the polymer therefore implies the presence of a thioether. The linker may also be an amino linker, e.g. $C-NRa-CH_2-$. The formula $-(C-S-CH_2)-$ allows that the

first C can be bound to one or two hydrogens or one or two carbon atoms or a mixture of C and H. For example, if 1,4-benzenedithiol is used, the S atom will be bound to the C of the benzene ring and CH₂ from the vinyl group. The C atom in -(C-S-CH₂)- may be double bonded to the next C in the chain, e.g. -C=CH-S-CH₂-. The group C-NRa-CH₂ allows that the first C can be bound to one or two hydrogens or one or two carbon atoms or a mixture of C and H.

If the two monomers are terminated in thiols then disulphides can be formed. Such disulphides are likely to be random copolymers of the monomers. It will be appreciated that disulphide formation is avoided when one monomer contains bithiol functionality by using reaction conditions/catalysis that promotes the desired monomer reaction, e.g. radical initiation promotes thiol ene reactions.

It will be essential that the monomer combination used results in the formation of a polymer containing ester groups in the backbone of the polymer. Thus, if monomer B' or D' is free of ester groups then monomer A' or C' will need to comprise ester groups and vice versa. For this reason, it is required that, monomers BI and DI react with an ester containing monomer A'. The skilled person can identify X, Y, W and Z groups that will react to form the defined linkers.

In any embodiment of the invention, alkyl or alkylene groups are preferably linear.

Both n' and m have values of 0 to 500 such as n' + m add to 1-500, more preferably 10-300, especially 15-100.

The term arylalkyl group is used herein to cover both benzyl type linkers (CH₂-Ph) where the bond is via the alkyl portion or methylphenyl type groups where the bond is via the aryl group.

By vinyl terminated, amine terminated or thiol terminated monomer is meant that the end groups on the monomer are vinyl (CH=CH₂ or CR=CH₂), amino -NRaH or thiol (SH) respectively. It will be appreciated that all monomers must comprise a minimum of two such groups. Preferably, vinyl terminated monomers are terminated in (meth)acryloxy groups, especially (meth)acryloxyalkyl groups.

The term polyester is used herein to refer to a monomer unit comprising a plurality of ester groups in the backbone of the molecule. Preferred monomer units are

based on a diester as the polyester. It is preferred if any polyester monomer is a diester monomer. A monomer containing two (meth)acryloxy groups contains two esters.

Detailed Description

5

This invention relates to a new binder for coating compositions, especially marine coating compositions. The new binder can be used in a fouling release coating composition or an anti-fouling coating composition. The fouling release composition is preferably free of anti-fouling agent and is formed from a coating composition comprising the binder of the invention, ideally via crosslinking of that composition. The term anti-fouling coating composition refers to a composition comprising the binder of the invention and at least one marine anti-fouling agent. The fact that the binder contains ester hydrolysable groups makes the binder ideal for use in either type of coating. The slow hydrolysis also allows regeneration of the coating surface. This regeneration effectively deals with the issue of algae/slime formation on a fouling release coating composition. The hydrolysis reaction allows controlled release of the anti-fouling agent in an anti-fouling coating.

15

We use the term coating composition below to refer to either anti-fouling or fouling release coating compositions.

20

The term binder is a term of this art. The binder is the actual film forming component of the coating composition. The coating composition comprises the binder as well as other components as discussed in detail below. The binder imparts adhesion and binds the components of the coating composition together.

25

The polymer binder of the invention is made up from multiple monomers, e.g. at least two monomers. In a first embodiment, there is at least one polysiloxane unit A' (which may be considered a polysiloxane monomer) and at least one other monomer unit (called the second monomer herein) B' or D', that reacts with the polysiloxane unit A' to generate a copolymer with a plurality of ester hydrolysable linkages in the polymer backbone. The polymer backbone is ideally one that contains the group – [CH₂-S-CH₂]- as well as a plurality of -COO- (or (OCO)) groups. The ester functional groups can derive from monomer A' or monomer B' or both.

30

The polymer is preferably of the type -ABABA- because it is formed by addition polymerisation and is not a block copolymer of the type AAABBBBBBAAA. It is the ester hydrolysable linkages that hydrolyse over time in seawater and allow regeneration of the surface of a fouling release coating and allow renewal and leaching of the biocide present in the anti-fouling composition of the invention.

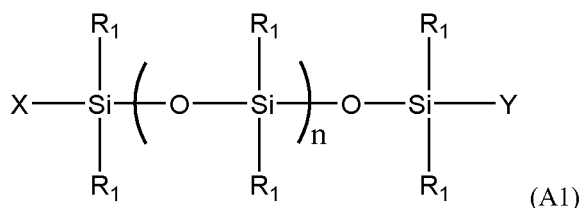
The backbone contains the hydrolysable linkage -O-CO-. Other hydrolysable linkages may also be present although preferably the only hydrolysable linker present is the ester group. Hydrolysable links may be present within the backbone of the polymerising units before polymerisation and hence become part of the copolymer backbone during polymerisation. Monomer A' or B' contains at least one ester hydrolysable group within the backbone of the monomer which will become part of the polymer backbone on copolymerisation.

It will be appreciated that the polysiloxane unit can act as the nucleophile or may act as the electrophile depending on the functional groups present. It may be easier to use the polysiloxane unit as a nucleophile but the invention could easily be adapted to place an electrophilic group at the end of the polysiloxane unit and allow attack on the polysiloxane unit by the second monomer. The polymerisation is preferably an addition polymerisation but other types of polymerisation familiar to the skilled person can also be used.

The crux of the invention is the appreciation that a valuable marine binder can be prepared by introducing hydrolysable linkages such as -O-CO- into the backbone of a polysiloxane polymer. This is achieved herein using monomers which are functionalised to carry thiol and vinyl end groups to develop disulphide or thiol linkages in the polymer. Alternatively, the monomers carry vinyl and amino end groups to develop an amino linkage in the polymer.

In any embodiment, it is preferred if one of the monomers A' or B' contains two ester groups.

The polysiloxane unit which is copolymerised to generate a binder of the invention is preferably of general formula (A1):



wherein each R_1 is the same or different and represents an unsubstituted or substituted C_{1-20} alkyl, C_{2-20} alkenyl, C_{3-20} cycloalkyl, C_{6-20} aryl, C_{7-20} arylalkyl group, or a polyoxyalkylene chain;

X and Y can be the same or different and represent $-\text{CR}=\text{CH}_2$, $-(\text{CR}'')_x-$, $\text{CR}=\text{CH}_2$, $-(\text{CR}'')_x-\text{CR}''_2-\text{OCO}-\text{CR}=\text{CH}_2$, $-\text{CR}''_2-\text{OCO}-\text{CR}=\text{CH}_2$, $-(\text{CR}'')_x-\text{SH}$; $-(\text{CR}'')_x-\text{O}-(\text{CR}'')_x-\text{SH}$, $-(\text{CR}'')_x-[\text{O}-(\text{CR}'')_x]_f-\text{OCO}-\text{CR}=\text{CH}_2$, $-(\text{CR}'')_x-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7-\text{SH}$, $-(\text{CR}'')_x-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7-\text{CR}=\text{CH}_2$, $-\text{CR}''_2-\text{Ar}-\text{CR}''_2-\text{SH}$, $-(\text{CR}'')_x-\text{C}\equiv\text{CH}$, $-(\text{CR}'')_x-\text{O}-(\text{CR}'')_x-(\text{CHOH})-(\text{CR}'')_x-\text{OCO}-\text{CR}=\text{CH}_2$ or $-(\text{CR}'')_x-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7-\text{C}\equiv\text{CH}$;

R'' is independently C_{1-6} alkyl or H, especially H;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

each R is independently H or Me;

where R^7 and R^8 are each independently C_{2-6} alkylene and $a = 0-50$, $b = 0-50$ and $a+b = 1-50$;

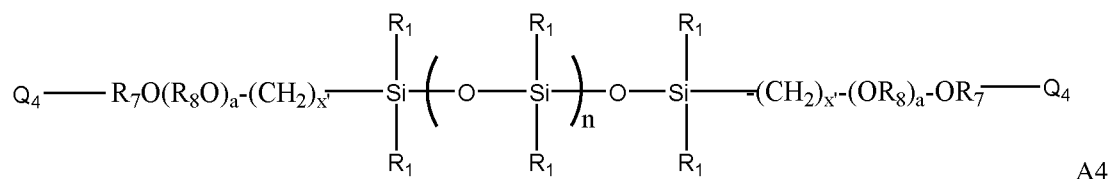
f is 1 to 50;

Ar is C_6-12 aryl; and

n is 1-500, more preferably 10-300, especially 15-100.

It is preferred if R_1 is C_{1-6} alkyl, especially Me. The use of polydimethylsiloxane (PDMS) is thus preferred.

In one embodiment, the monomer A' is of formula A4



wherein the substituent groups are as hereinbefore defined, Q4 is (meth)acrylate and a= 0-50.

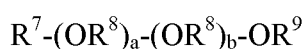
In monomer A', it is preferred if X and Y can be the same or different. It is preferred if X and Y represent -CR=CH₂, -(CH₂)_x-CR=CH₂, -(CH₂)_x-CH₂-OCO-CR=CH₂, -CH₂-OCO-CR=CH₂, -(CH₂)_x-SH; -(CH₂)_x-O-(CH₂)_x-SH, -(CH₂)_x-O-(CH₂)_x-OCO-CR=CH₂, -(CH₂)_x-(OR⁸)_a-(OR⁸)_b-OR⁷-SH, -(CH₂)_x-(OR⁸)_a-(OR⁸)_b-OR⁷-CR=CH₂, -CH₂-Ar-CH₂-SH, -(CH₂)_x-C≡CH, -(CH₂)_x-O-(CH₂)_x-(CHOH)-(CH₂)_x-OCO-CR=CH₂ or -C≡CH.

It is more preferred, in monomer A', if X and Y represent -CH=CH₂, -(CH₂)_x-CH=CH₂, -(CH₂)_x-CH₂-OCO-CR=CH₂, -CH₂-OCO-CR=CH₂, -(CH₂)_x-O-(CH₂)_x-(CHOH)-(CH₂)_x-OCO-CR=CH₂ or -(CH₂)_x-SH.

It is especially preferred, in monomer A', if X and Y represent -CH=CH₂, -(CH₂)_x-CH=CH₂, -(CH₂)_x-CH₂-OCO-CH=CH₂, -CH₂-OCO-CH=CH₂, -(CH₂)_x-CH₂-OCO-CMe=CH₂, -CH₂-OCO-CMe=CH₂, -(CH₂)_x-SH or -(CH₂)₃-O-(CH₂)₃-(CHOH)-(CH₂)₃-OCO-CR=CH₂.

It is especially preferred in monomer A', if X and Y represent -CH=CH₂, -(CH₂)_x-CH=CH₂, -(CH₂)_x-CH₂-OCO-CH=CH₂, -CH₂-OCO-CH=CH₂, -(CH₂)_x-CH₂-OCO-CMe=CH₂, -CH₂-OCO-CMe=CH₂, -(CH₂)_x-SH or -(CH₂)₃-O-(CH₂)₃-(CHOH)-(CH₂)₃-OCO-CR=CH₂ where x' is 1 to 5.

It is preferred if all R₁ groups are the same. It is preferred if R₁ is C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₆₋₂₀ aryl, C₇₋₂₀ arylalkyl. It is preferred if R₁ is unsubstituted. It is preferred if R₁ is a C₁₋₆ alkyl group such as ethyl or especially methyl. The use of a PDMS is therefore especially preferred. It is also possible however for at least one R₁ group to be a polyoxyalkylene chain. The molecule is likely to contain a plurality of these groups distributed across the polysiloxane backbone. The presence of such a chain enhances the hydrophilicity of the molecule. A suitable polyoxyalkylene chain may be one of formula:



where R⁷ and R⁸ are each independently C₂₋₆ alkylene and R⁹ is H, CH₃CO-, CH₃CH₂CO-, HCO-, or C₁₋₆ alkyl and a= 0-50, b= 0-50 and a+b = 1-50. It is preferred

if R⁹ is not H to avoid any reaction of the side chain. R⁹ is preferably CH₃CO-, CH₃CH₂CO-, HCO-, or C₁₋₆alkyl, especially CH₃CO- or CH₃CH₂CO-.

Thus, suitable materials include those selected from polyoxyethylene, polyoxypropylene and poly(oxyethylene-co-oxypropylene).

5 A preferred polysiloxane monomer is based on polydimethylsiloxane (PDMS). The end groups X and Y are preferably the same.

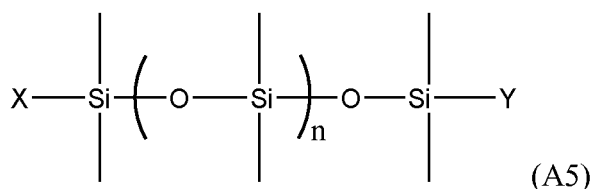
It is preferred if all R'' groups are the same. It is preferred if R'' is H.

It is especially preferred, in monomer A' if X and/or Y are -CH=CH₂, -(CH₂)_x-CH=CH₂, -(CH₂)_x-CH₂-OCO-CH=CH₂, -CH₂-OCO-CH=CH₂, -(CH₂)_x-CH₂-OCO-CMe=CH₂, -CH₂-OCO-CMe=CH₂, or -(CH₂)_x-SH. It is especially preferred in
10 monomer A', if X and Y are (meth)acryloxypropyl.

In a preferred option, the number average molecular weight (Mn) of the polysiloxane monomer A' may be at least 700, such as at least 1200, such as at least 2000. An upper limit of 40,000 such as 20,000, e.g. 17,000 is appropriate, such as at
15 most 15,000.

In theory, a branched polysiloxane monomer could be used in which therefore there are more end groups than just X and Y identified in formula (A') above. The use of a branched structure allows the generation of a branched copolymer with the second monomer. It is believed however, that the use of a bifunctional polysiloxane containing
20 essentially two reactive ends groups is preferred as such a monomer allows the generation of an essentially linear polymer. Any polymer of the invention will contain at least two residues derived from a polysiloxane unit.

A preferred polysiloxane monomer A' is therefore of formula (A5):



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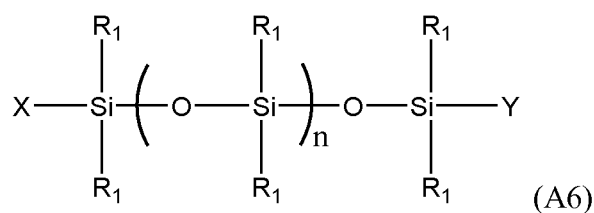
wherein,

X and Y are the same and represent $-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{O}-(\text{CH}_2)_x-(\text{CHOH})-(\text{CH}_2)_x-\text{OCO}-\text{CR}=\text{CH}_2$ or $-(\text{CH}_2)_x-\text{SH}$;

x' is 1 to 10, especially 2 to 5, such as 3 to 5; and

5 n is 10-300, especially 15-100.

A preferred polysiloxane monomer A' is therefore of formula (A6):



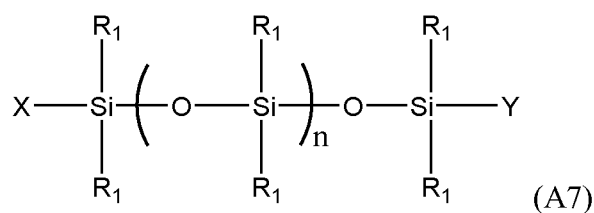
10 wherein each R_1 is methyl,

X and Y are the same and represent $-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_x-(\text{CHOH})-(\text{CH}_2)_x-\text{OCO}-\text{CR}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$ or $-(\text{CH}_2)_x-\text{SH}$;

x' is 1 to 5; and

15 n is 15-300.

A more preferred polysiloxane monomer A' is therefore of formula (A7):



20 wherein each R_1 is methyl,

X and Y are the same and are $-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-(\text{CH}_2)_x-\text{SH}$;

x' is 1 to 5, especially 2 to 5, such as 3 to 5; and

25 n is 15-100.

Potential siloxane monomers A' that may be used include:

Methacryloxypropyl terminated PDMS;

(3-Acryloxy-2-hydroxypropoxypropyl) terminated PDMS;

Acryloxy terminated ethyleneoxide-dimethylsiloxane-ethyleneoxide, (ABA type
5 block copolymer);

Vinyl terminated PDMS,

In order to manufacture the binder of the invention, the polysiloxane monomer
A' is ideally reacted with at least one further monomer B' or D'. This is the second
monomer. The reaction between the two monomers generally occurs via the reaction
10 of a thiol on one monomer with a vinyl group on the other monomer or via two thiols to
form a disulphide link. In a second embodiment, the reaction occurs via an amine and a
vinyl group.

In the first embodiment therefore, the reaction may therefore be a thiol ene
reaction or a Michael addition. The skilled person will appreciate that the thiol group
15 can be present on either monomer as long as the other monomer contains a reactive
group capable of reacting with the thiol group in a polymerisation reaction.

It is also essential that the formed polymer contains ester groups in its backbone.
These can derive from the monomer B', monomer A' or both.

It is preferred to use a multifunctional second monomer in an addition
20 copolymerisation reaction with the polysiloxane monomer A'. In such an addition
polymerisation reaction, the two "monomers" preferably react to generate a copolymer
having the structure -[ABAB]- in which an ester hydrolysable linkage is present. In
essence therefore the end group of the polysiloxane monomer A' reacts with the end
group of the second monomer B' to generate a link (normally C-NRa-CH₂ or C-S-
25 CH₂), e.g. via ene or Michael addition chemistry. The resulting polymer comprises
ester groups that hydrolyse in sea water and therefore ensures that the binder of the
invention is one that self polishes.

Monomer B'

30

The second monomer B' is preferably of lower molecular weight than the
polysiloxane unit so that the majority, by weight, of the binder polymer is formed from

the polysiloxane residues. It is therefore preferred if the number average Mn of the second monomer B' is less than 2,000, such as less than 1,000, especially less than 500, such as less than 400.

The Mn of the monomer B' is preferably less than 2,000, such as less than 1,000, especially less than 500, such as less than 300.

In theory, a branched monomer B' could be used in which therefore there are more end groups than just W and Z identified in formula (B') above. The use of a branched structure allows the generation of a branched copolymer with the first monomer. It is believed however, that the use of a bifunctional monomer B' containing essentially two reactive ends groups is preferred as such a monomer allows the generation of an essentially linear polymer.

Preferred Monomers B' - Thiols

In one embodiment, the polysiloxane monomer A' comprises suitable vinyl end groups/S_H groups and the necessary ester linkages. In such an embodiment, preferred monomers B' are thiols of formula (BI):



20

wherein Q3 is C2-20 alkyl, C3-20 cycloalkyl, phenyl, biphenyl, terphenyl, C7-20 alkylaryl group, alkyl-polysiloxane-alkyl, C4-20 alkylcycloalkyl or polyether wherein said C2-20 alkyl, C3-20 cycloalkyl, C7-20 alkylaryl group, or C4-20 alkylcycloalkyl optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

25

with the proviso that the S_H groups in monomer B' react with the X and Y groups in ester containing monomer A' to form a group C-S-CH₂ or S-S group.

The S_H groups in this monomer B' are preferably selected to react with vinyl X and Y groups in monomer A' to form a group -C-S-CH₂.

30

It is preferred if Q3 represents a C2-16 alkylene, alkyl-polysiloxane-alkyl, phenyl, tolyl, or biphenyl group.

Where Q3 represents a phenyl group, the –SH groups are ideally positioned 1,3 or 1,4 on the ring. If the Q3 group is a tolyl group, the SH groups are ideally bound to the phenyl ring rather than the alkyl side group.

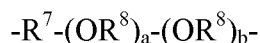
If Q3 represents alkyl-polysiloxane-alkyl, said alkyl groups may be C1-6 alkyls.
 5 The polysiloxane is ideally a PDMS. It may have n repeating units where n is 1 to 100.

It is preferred if the compound of formula (BI) is aliphatic. It is preferred if Q3 is a C2-12 alkylene or a polyether.

Where Q3 represents a polyether, this must contain at least two ether linkages. Ideally, these ether linkages derive from ethylene glycol units. The monomer B' may
 10 contain 2 to 10 such units. It will be appreciated that the SH group cannot bind directly to the O of the polyether and hence there will always be an alkyl linkage between the O of the polyether and the SH, typically an ethyl linkage or methyl linkage.

It is also possible to use a polyether such that the monomer B' may have a Mn in the range of 800 to 10,000, such as 1,000 to 8,000. This can be achieved using a
 15 PEG group.

Q3 may therefore be a polyether of formula



20 where R^7 and R^8 are each independently C_{2-6} alkylene and $a=0-50$, $b=0-50$ and $a+b=1-50$.

A preferred monomer B' is therefore



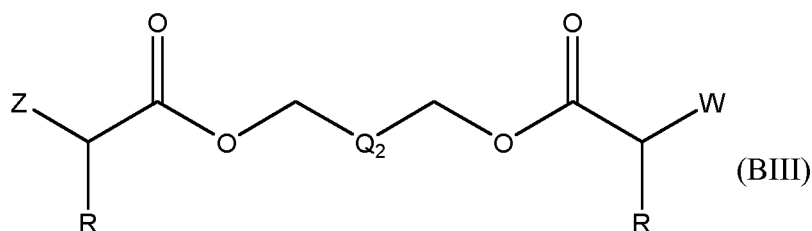
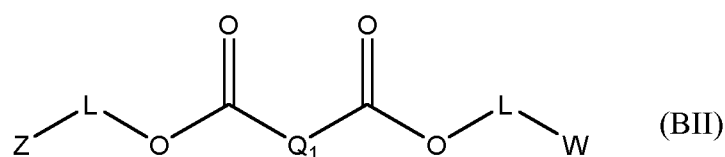
25 wherein Q3 is a C2-16 alkylene, alkyl-polysiloxane-alkyl, or polyether group.

Suitable thiols as monomer BI and BIV are 1,2-Ethanedithiol; 1,3-Propanedithiol; 1,4-Butanedithiol; 1,6-Hexanedithiol; 1,8-Octanedithiol; 1,9-Nonanedithiol; 1,11-Undecanedithiol; 1,16-Hexadecanedithiol; 2,2'-(Ethylenedioxy)diethanethiol; Tetra(ethylene glycol) dithiol; Hexa(ethylene glycol)
 30 dithiol; Toluene-3,4-dithiol; 1,3-Benzenedithiol; 1,4-Benzenedithiol; 1,4-Benzenedimethanethiol; Biphenyl-4,4'-dithiol

p-Terphenyl-4,4''-dithiol; Poly(ethylene glycol) dithiol, e.g. Average Mn 1,000; Poly(ethylene glycol) dithiol, e.g. Average Mn 1,500; Poly(ethylene glycol) dithiol, e.g. Average Mn 3,400; Poly(ethylene glycol) dithiol, e.g. Average Mn 8,000.

These thiol monomers B' are therefore combined with a monomer A' in which polysiloxane and ester linkages are present and which comprise a reactive vinyl group or SH group.

Monomer B' may also be of formula (BII) or (BIII):



10

wherein Q1 represents a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, a polyoxyalkylene chain of formula $\text{R}^7-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7$, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C4-10 alkylcycloalkyl; wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups, optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

15

L is C1-20 alkylene optionally comprising one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O or N, or a polyoxyalkylene chain of formula:

20



where R^7 and R^8 are each independently C_{2-6} alkylene and $a = 0-50$, $b = 0-50$ and $a+b = 1-50$;

R is H or Me;

Q2 is a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

W and Z are $-SH$, $-(CR''_2)_xSH$, $CH_2=CR-$, $CH_2=CR-(CR''_2)_{x'}-$, $-C\equiv CH$, $-NHCH_2-CR=CH_2$, $NHCH_2-CR\equiv CH-NHRa$, $-NHRa$ or W and Z are $=CH_2$ (thus forming a double bond with the C atom to which W/Z is attached);

Ra is H or C1-6 alkyl wherein said alkyl group optionally comprises one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

R'' is independently C_{1-6} alkyl or H, especially H;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

with the proviso that the W and Z groups in monomer B' react with the X and Y groups in monomer A' to form a group C-S-CH₂ or S-S group.

If the monomer B' is of formula BII, it is preferred if it is terminated in a vinyl or alkynyl group. In this scenario, the polysiloxane contains the necessary thiol group.

Q1 is preferably C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, or C4-10 alkylcycloalkyl.

More preferably, Q1 is C2-10 alkyl, C3-8 cycloalkyl, C3-8 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, or C4-10 alkylcycloalkyl.

Q2 is preferably a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl.

Q2 is more preferably a covalent bond, C1-10 alkyl, C3-8 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl.

L is preferably C1-10 alkylene, such as C1-5 alkylene or a polyoxyalkylene chain of formula:

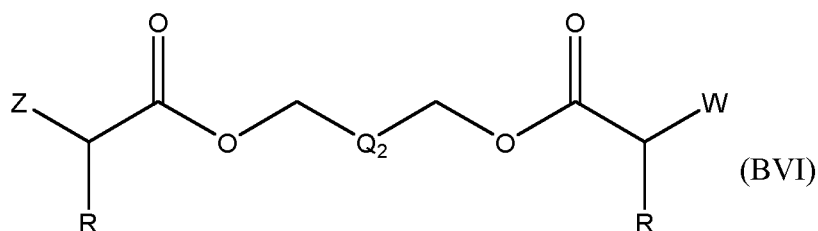
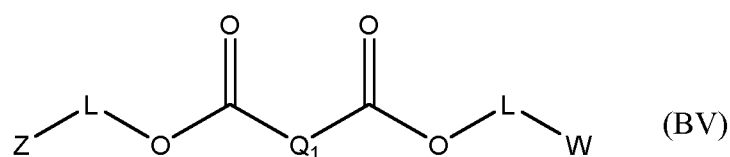


where R^7 and R^8 are each independently C_{2-6} alkylene and $a = 0-50$.

W and Z are preferably $-\text{SH}$, $-\text{CH}_2-\text{SH}$, $\text{CH}_2=\text{CR}-$; $\text{CH}_2=\text{CR}-\text{CH}_2-$ or W and Z are $=\text{CH}_2$. W and Z are more preferably $-\text{SH}$, $-\text{CH}_2-\text{SH}$, $\text{CH}_2=\text{CR}-$; or $\text{CH}_2=\text{CR}-\text{CH}_2-$. W and Z are more preferably $\text{CH}_2=\text{CR}-$; or $\text{CH}_2=\text{CR}-\text{CH}_2-$.

In one embodiment L comprises N heteroatoms in its backbone. L is thus -
 5 $(\text{CH}_2)_{x'}-\text{NH}-(\text{CH}_2)_x$, wherein x' is independently 1 to 5. In one embodiment the L group is a polyoxyalkylene chain and W and Z are $-\text{NHCH}_2-\text{CR}=\text{CH}_2$.

Preferred monomers B' are therefore of formula BV or BVI



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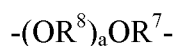
wherein Q1 is C2-10 alkyl, C3-8 cycloalkyl, C3-8 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, or C4-10 alkylcycloalkyl;

Q2 is a covalent bond, C1-10 alkyl, C3-8 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl;

15

R is Me or H;

L is preferably C1-10 alkylene, such as C1-5 alkylene or a polyoxyalkylene chain of formula:

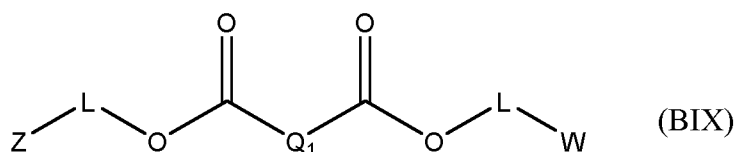


20

where R^7 and R^8 are each independently C_{2-6} alkylene and $a = 0-50$;

W and Z are $-\text{SH}$, $-\text{CH}_2-\text{SH}$, $\text{CH}_2=\text{CR}-$; $\text{CH}_2=\text{CR}-\text{CH}_2-$, or W and Z are $=\text{CH}_2$.

Preferred monomers B' are therefore of formula BIX

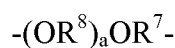


5 wherein Q₁ is C₂-10 alkyl, C₃-8 cycloalkyl, C₃-8 cycloalkenyl, C₆-10 aryl, C₇-12arylalkyl, or C₄-10 alkylcycloalkyl;

R is Me or H;

L is preferably C₁-10 alkylene, such as C₁-5 alkylene or a polyoxyalkylene chain of formula:

10



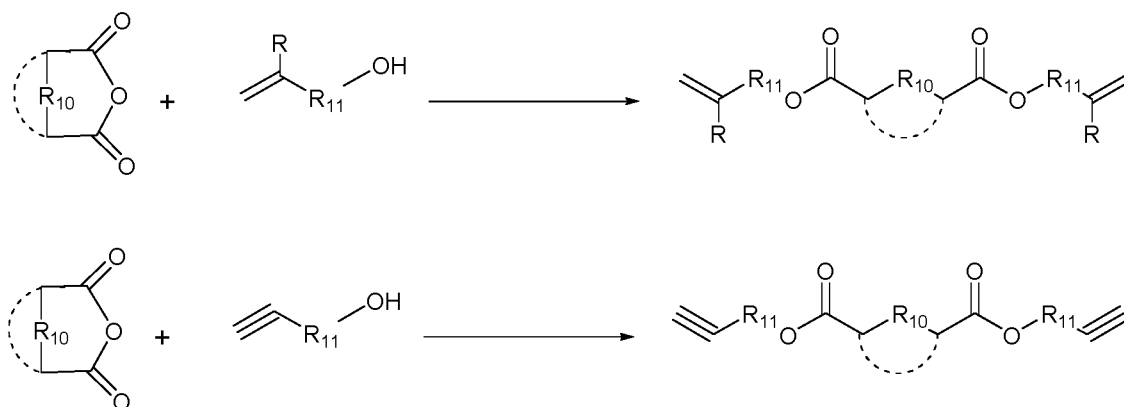
where R⁷ and R⁸ are each independently C₂₋₄ alkylene and a = 0-50;

W and Z are -SH, -CH₂-SH, CH₂=CR-; CH₂=CR-CH₂-, or W and Z are =CH₂.

15

It is especially preferred to combine monomers A5-A7 with BIV to BVI or BIX.

Suitable monomers (BII) can be, for example, synthesized from a cyclic anhydride and a vinyl alcohol or propargyl alcohol as illustrated in the scheme below:



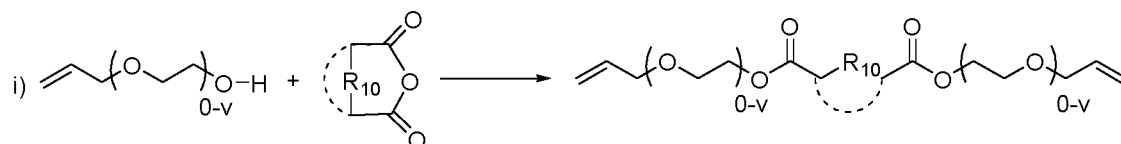
20

In these compounds R₁₀ represents a group forming a ring. Preferably R₁₀ is a, C₁-8 alkyl or R₁₀ together with the carbon atoms to which it is attached forms a C₆-10 aromatic ring or C₃-10 cyclic ring fused to the anhydride ring (thus creating a bi-ring system). R₁₀ is preferably a C₁-4 alkyl or together with the carbon atoms to which it is

attached forms a 6-membered aromatic ring or 5 to 6 membered aliphatic cyclic ring (e.g. a C6 alkenyl ring).

In the vinyl alcohol component R is H or Me. R₁₁ is a C1-6 alkyl. R₁₁ may be a linear or branched C1-6 alkyl. Other possible vinyl alcohols are mentioned below.

5 The reaction may also involve an ether containing allyl reactant:

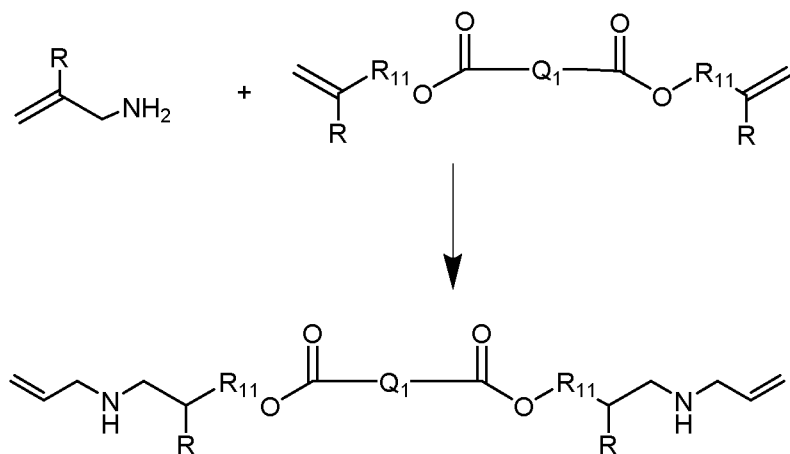


v is preferably 1 to 10, such as 1 to 3.

Suitable reactants for these processes are: Anhydrides: succinic anhydride, Methylsuccinic anhydride, Glutaric anhydride, Phthalic anhydride, 3,4,5,6-
10 Tetrahydrophthalic anhydride, Homophthalic anhydride, 3,3-Dimethylglutaric anhydride.

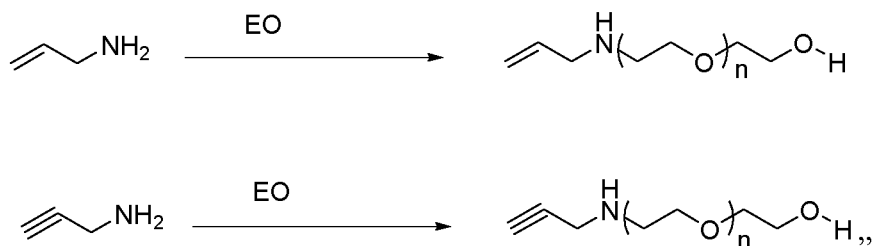
Suitable vinyl alcohols include: Allyl alcohol; 2-Methyl-2-propen-1-ol; 3-Buten-2-ol, Diethylene glycol monoallyl ether.

15 The person skilled in the art knows other routes to obtain monomers B' type monomers. For example, amino containing monomers may be made via the following scheme:



wherein Q1, R and R₁₁ are as hereinbefore defined

20 Allyl amine or propargyl amine may also be prereacted with ethylene oxide units to create alkene/alkyne functional polyether's.



In a second embodiment, the monomer B' can be formed from a dicarboxylic acid or derivative thereof:



wherein Q1 is as hereinbefore defined such as C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12 arylalkyl or C4-10 alkylcycloalkyl. The skilled person will appreciate that the carboxylic acid can be converted to its corresponding ester or acid halide to help this reaction as required.

In one embodiment, a monomer B' can be prepared from the reaction of a mercaptoalcohol with a diacid or derivative thereof as illustrated in the scheme below:



where R₁₃ is C2-20 alkyl, C2-20 ether or a polyether such as a polyethylene glycol-alkyl group;

Q1 is as hereinbefore defined. If R₁₃ represents a polyethylene glycol that is preferably of formula -R7-(OR8)_a-(OR8)_b-

where R7 and R8 are each independently C2-6 alkylene and a= 0-50, b= 0-50 and a+b = 1-50.

Suitable dicarboxylic acids include malonic acid; Succinic acid; Glutaric acid; Adipic acid; Sebacic acid; 1,3-Bis(4-carboxyphenoxy)propane, Pimelic acid; Benzene-1,4-dicarboxylic acid; 1,4-Cyclohexanedicarboxylic acid; Poly(ethylene glycol) bis(carboxymethyl) ether, average Mn 250; Poly(ethylene glycol) bis(carboxymethyl) ether, average Mn 600.

Suitable mercaptoalcohols include Mercaptoalcohols, 2-Mercaptoethanol,

3-Mercapto-1-propanol, 4-Mercapto-1-butanol, 6-Mercapto-1-hexanol, 8-Mercapto-1-octanol, 11-Mercapto-1-undecanol, 2-{2-[2-(2-Mercaptoethoxy)ethoxy]ethoxy}ethanol.

In an especially preferred embodiment, the polymer is the reaction product of a (meth)acryloxyalkyl terminated polysiloxane monomer and a bithiol monomer, such as a thiol terminated polyester monomer.

In an especially preferred embodiment, the polymer is the reaction product of a thiol terminated polysiloxane monomer and a vinyl terminated polyester monomer.

In an especially preferred embodiment, the polymer is the reaction product of a vinyl terminated polysiloxane monomer and a thiol terminated polyester monomer.

In one embodiment, the polymer is the reaction product of a thiol terminated polysiloxane monomer and a thiol terminated polyester polyol monomer.

Amine Aspects:

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In a second aspect the invention concerns binders in which the polymer is obtained from the reaction of an amine monomer with a vinyl or alkynyl terminated monomer such as a (meth)acrylate terminated polysiloxane and an amine monomer.

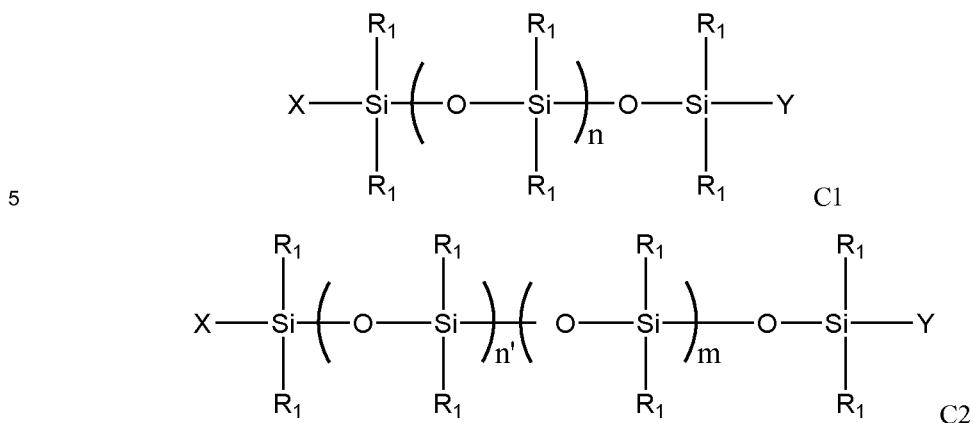
In an especially preferred embodiment, the polymer is the reaction product of a (meth)acryloxyalkyl terminated polysiloxane monomer and an amine terminated monomer, such as an amine terminated polyester monomer.

In another preferred embodiment, the polymer is the reaction product of an amine functionalised polysiloxane monomer and a vinyl terminated polyester monomer.

In a preferred embodiment, the polymer is the reaction product of a (meth)acryloxyalkyl terminated polysiloxane monomer and an amine terminated polysiloxane monomer.

Insofar as the polysiloxane monomer is a (meth)acryloxyalkyl terminated polysiloxane monomer, such monomers are described above in detail as monomer A'. Certain especially preferred (meth)acryloxyalkyl terminated polysiloxane monomers are described further below. In a further embodiment, such a monomer can be amine terminated. These will be called monomer C' herein.

Viewed from another aspect the invention provides a binder for a marine coating composition comprising the reaction product of at least one polysiloxane monomer C' of general formula (C1)-(C2):



wherein each R₁ is the same or different and represents an unsubstituted or substituted C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₃₋₂₀ cycloalkyl, C₆₋₂₀ aryl, C₇₋₂₀ arylalkyl group, or a polyoxyalkylene chain;

X and Y can be the same or different and represent -(CR'')_x-NRaH, -(CR'')_x-NH-(CR'')_x-NRaH, -(CR'')_x-O-(C₁₋₆ alkyl)_x-NRaH, -(CR'')_x-O-(CR'')_x-NRaH or -CR'')₂-Ar-CR'')₂-NH₂ wherein said alkyl group can be interrupted by heteroatoms;

R'' is independently C₁₋₆ alkyl or H, especially H;

Ra is H or C₁₋₆ alkyl;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5; and

n is 1-500, more preferably 10-300, especially 15-100;

or n' + m add to 1-500, more preferably 10-300, especially 15-100.

In preferred monomers C', R₁ is methyl. The use of PDMS is again preferred in this aspect. It is preferred if X and Y are the same.

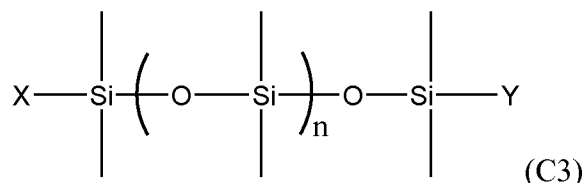
In preferred monomers C', X and Y are represent -(CH₂)_x-NRaH,

-(CH₂)_x-NH-(CH₂)_x-NRaH, -(CH₂)_x-O-(CH₂)_x-NRaH, -(CH₂)_x-(O-C₁₋₆ alkyl)_x-NRaH, -CH₂-Ar-CH₂-NH₂. More preferably, X and Y are -(CH₂)_x-NRaH.

Ra is preferably H. Thus the most preferred X and Y groups in monomer C' are -(CH₂)_x-NH₂, -(CH₂)_x-NH-(CH₂)_x-NH₂, -(CH₂)_x-O-(CH₂)_x-NH₂, -(CH₂)_x-O-(CH₂CH(CH₃))_x-NH₂.

Preferred amine monomers C' include alpha, omega-amino (prim. and sec.) functional siloxanes with a total chain length of 10 – 100.

Preferred monomers C' are



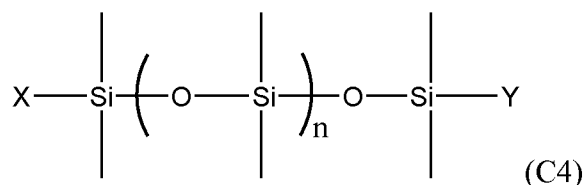
wherein X and Y are the same and represent $-(\text{CH}_2)_{x'}-\text{NRaH}$, $-(\text{CH}_2)_{x'}-\text{NH}-(\text{CH}_2)-\text{NRaH}$, $-(\text{CH}_2)_{x'}-\text{O}-(\text{CH}_2)_{x'}-\text{NRaH}$, $-(\text{CH}_2)_{x'}-\text{O}-(\text{C}_{2-6} \text{ alkyl})_{x'}-\text{NRaH}$, $-\text{CH}_2-\text{Ar}-\text{CH}_2-\text{NH}_2$, especially X and Y are $-(\text{CH}_2)_{x'}-\text{NRaH}$

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

Ra is H or C1-6 alkyl; and

n is 1-500, more preferably 10-300, especially 15-100; or n' + m add to 1-500, more preferably 10-300, especially 15-100.

Preferred monomers C' are

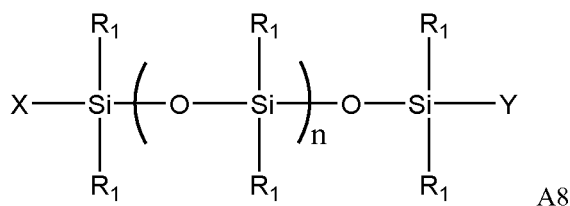


X and Y groups are the same and are $-(\text{CH}_2)_{x'}-\text{NH}_2$, $-(\text{CH}_2)_{x'}-\text{NH}-(\text{CH}_2)_{x'}-\text{NH}_2$, $-(\text{CH}_2)_{x'}-\text{O}-(\text{CH}_2)_{x'}-\text{NH}_2$, $-(\text{CH}_2)_{x'}-\text{O}-(\text{CH}_2 \text{ CH}(\text{CH}_3))_{x'}-\text{NH}_2$;

x' is 1 to 5; and

n is 1-500, more preferably 10-300, especially 15-100.

In a preferred embodiment, when the second monomer is an amine D', monomer A' comprises a (meth)acryloxyalkyl group. Preferred monomers A' are of general formula (A8):



wherein each R₁ is the same or different and represents an unsubstituted or substituted C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₃₋₂₀ cycloalkyl, C₆₋₂₀ aryl, C₇₋₂₀ arylalkyl group, or a polyoxyalkylene chain;

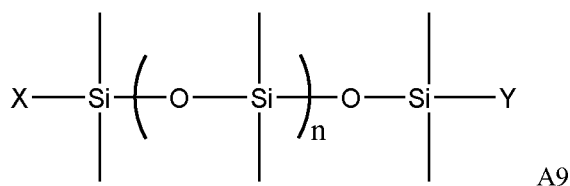
X and Y can be the same or different and represent -(CH₂)_x-CH₂-OCO-CR=CH₂, or -CH₂-OCO-CR=CH₂;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

each R is independently H or Me; and

n is 1-500, more preferably 10-300, especially 15-100.

More preferably, monomer A'



wherein X and Y can be the same or different and represent -(CH₂)_x-CH₂-OCO-CR=CH₂, or -CH₂-OCO-CR=CH₂;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

each R is independently H or Me; and

n is 1-500, more preferably 10-300, especially 15-100.

Preferred monomers C' are amine terminated PDMS e.g. Tegomer® A-Si 2122, Tegomer® A-Si 2322.

Where the polysiloxane monomer A' is vinyl terminated such as with (meth)acryloxyalkyl group, then to form an amine link, the second monomer must be an amine terminated monomer.

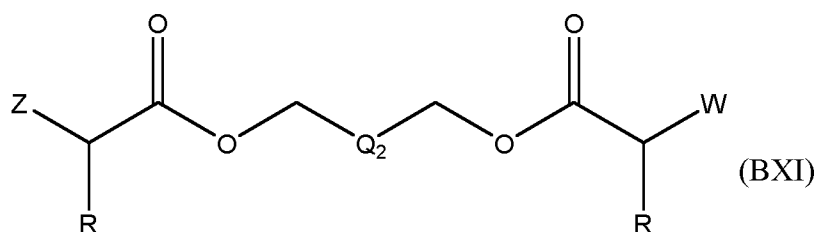
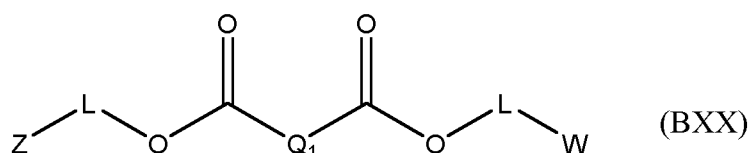
In one embodiment, the monomer is monomer D' of formula



wherein Q5 is C2-20 alkyl, C2-20 alkenyl, C3-20 cycloalkyl, phenyl, biphenyl, Ph-O-Ph, terphenyl, C7-20 alkylaryl group, alkyl-polysiloxane-alkyl, C4-20 alkylcycloalkyl, heterocycyl or polyether wherein said C2-20 alkyl, C3-20 cycloalkyl, C7-20 alkylaryl group, or C4-20 alkylcycloalkyl optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

Ra is H or C1-6 alkyl;

with the proviso that the amine groups in monomer D' react with the X and Y groups in ester containing monomer A'. Alternatively, when monomer C' is employed, it is preferably combined with a monomer D' of formula (BXX) or (BXI)



wherein Q1 represents a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, a polyoxyalkylene chain of formula $\text{R}^7-(\text{OR}^8)_a-(\text{OR}^8)_b-\text{OR}^7$, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C4-10 alkylcycloalkyl; wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl, optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

L is C1-20 alkylene optionally comprising one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O or N, or a polyoxyalkylene chain of formula:



where R^7 and R^8 are each independently C_{2-6} alkylene and $a = 0-50$, $b = 0-50$ and $a+b = 1-50$;

5 R is H or Me;

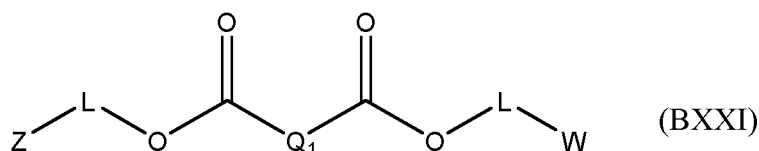
Q_2 is a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl wherein said C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

10 W and Z are $CH_2=CR-$; $CH_2=CR-CH_2-$, $-NHCH_2-CR=CH_2$, $-C\equiv CH$, or W and Z are $=CH_2$ (thus forming a double bond with the C atom to which W/Z is attached);

R_a is H or C1-6 alkyl;

with the proviso that the W and Z groups in monomer B' react with the amino X and Y groups in monomer C' to form a C-N R_a -CH₂- group.

15 Alternatively, when monomer C' is employed, it is preferably combined with a monomer D' of formula (BXXI)



20 wherein Q_1 is C2-10 alkyl, C3-8 cycloalkyl, C3-8 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, or C4-10 alkylcycloalkyl;

L is preferably C1-10 alkylene, such as C1-5 alkylene or a polyoxyalkylene chain of formula:



where R^7 and R^8 are each independently C_{2-4} alkylene and $a = 0-50$; and

R is H or Me;

30 W and Z are $CH_2=CR-$; $CH_2=CR-CH_2-$, $-NHCH_2-CR=CH_2$, $-C\equiv CH$, or W and Z are $=CH_2$ (thus forming a double bond with the C atom to which W/Z is attached);

with the proviso that the W and Z groups in monomer B' react with the amino X and Y groups in monomer C' to form a C-NRa-CH₂- group.

It is especially preferred if D' represents

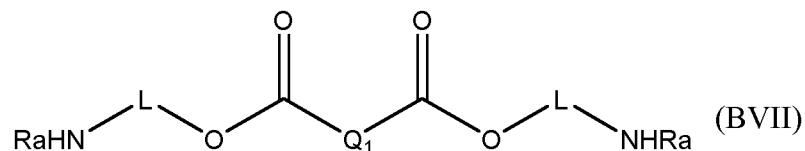


wherein Q5 is C₂-10 alkyl, C₁₋₆alkyl-polysiloxane-C₁₋₆alkyl;

Ra is H or C₁₋₆ alkyl. The polysiloxane component is ideally PDMS. This is ideally reacted with monomer A8 or A9.

Possible amine reagents are: Ethylenediamine; 1,3-Diaminopropane; Hexamethylenediamine; m-Xylylenediamine; 2,2'-Biphenyldiamine; 4,4'-Oxydianiline, N,N'-Diethyl-2-butene-1,4-diamine; 1,2,4-Thiadiazole-3,5-diamine; Poly(ethylene glycol) diamine, Mn 2000; Poly(ethylene glycol) diamine, Mn 3000; Poly(ethylene glycol) diamine, Mn 6,000; Poly(ethylene glycol) diamine, Mn 10,000.

When combined with a vinyl terminated monomer A', monomer B' may be of formula (BVII)



wherein Q₁ represents C₁-20 alkyl, C₃-10 cycloalkyl, C₃-10 cycloalkenyl, C₆-10 aryl, C₇-12arylalkyl, a polyoxyalkylene chain of formula R⁷-(OR⁸)_a-(OR⁸)_b-OR⁷, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C₄-10 alkylcycloalkyl; wherein said C₁-20 alkyl, C₃-10 cycloalkyl, or C₃-10 cycloalkenyl, optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

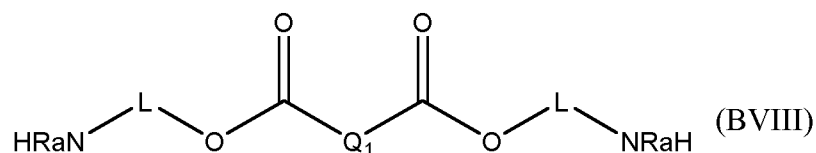
L is C₁-20 alkyl, a polyoxyalkylene chain of formula:



where R⁷ and R⁸ are each independently C₂₋₆ alkylene and a= 0-50, b= 0-50 and a+b = 1-50; and

Ra is H or C1-6 alkyl.

Preferred monomers B' are therefore of formula BVIII

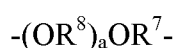


5

wherein Q1 is C2-10 alkyl, C3-8 cycloalkyl, C3-8 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, or C4-10 alkylcycloalkyl;

L is preferably C1-10 alkylene, such as C1-5 alkylene or a polyoxyalkylene chain of formula:

10



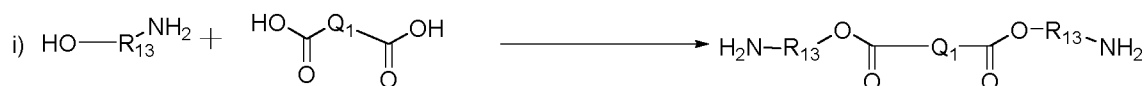
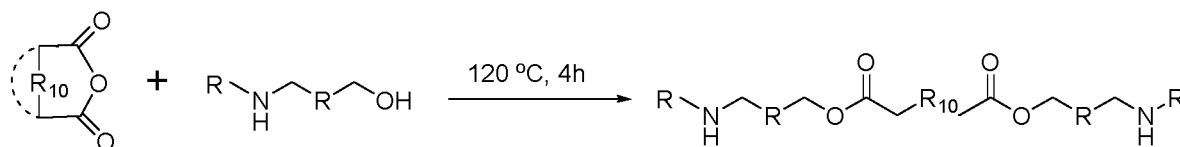
where R⁷ and R⁸ are each independently C₂₋₄ alkylene and a= 0-50; and

15

Ra is H or C1-6 alkyl.

Suitable reagents of formula BVII/BVIII can be made analogously to thiol reactants above. For example a cyclic anhydride (e.g. as described above) can react with an amino alcohol:

20



25

where R₁₀ and R₁₃ are as hereinbefore defined.

Suitable amine alcohols are 2-(Methylamino)ethanol, 2-(Ethylamino)ethanol, 3-Methylamino-1-propanol, N-(2-Hydroxyethyl)aniline, 2-Benzylaminoethanol.

Suitable reagents include Succinic anhydride, Methylsuccinic anhydride, Glutaric anhydride, Pthalic anhydride, 3,4,5,6-Tetrahydrophthalic anhydride, Homophthalic anhydride, 3,3-Dimethylglutaric anhydride, Dimethyl succinate, Dimethyl adipate, Diethyl succinate, Dimethyl terephthalate, Dimethyl cyclohexane-
5 1,4-dicarboxylate.

Introduction of polyether

In a preferred embodiment, the monomers are designed so that one of them introduces a polyether group into the backbone of the molecule, e.g. a polyethylene glycol or polypropylene glycol type group. The incorporated poly(oxyalkylene) such
10 as PEG, PPG might have a Mn: 50-5,000, such as 50-2,000, more preferably less than 1,000 . Preferably PEG with 1-100, more preferably 1-50, especially 2-30 repeating units is used.

The presence of the polyether will help regulate the water-uptake of the polymer film formed using the binder and may add hydrogel-like properties with PEG giving
15 inertness towards protein adsorption.

In a preferred option therefore, the monomer B' comprises an ethylene glycol or propylene glycol repeating unit.

Thus the monomer B' might comprise the residue of a PEG or PPG molecule.

The explanations above allow the person skilled in the art to design a variety of
20 binders that meet the requirements of the functional definitions in the claims.

Binder

It will be appreciated that devising a general formula to cover all possible
25 options is difficult.

The binder of the invention preferably has a number average molecular weight Mn of 2,000 to 100,000 such as 5,000 to 80,000, especially 10,000 to 50,000.

The binder of the invention has a very low glass transition temperature, such as 0°C or less, preferably -50°C or less, especially -100°C or less.

30

End Capping

The polymer may have end groups represented by F and G. Groups F and G are as defined above for X and Y (or W and Z) or groups F and G can be derived via a post polymerisation end capping or end modifying of the copolymer. By end capping/end modifying, we mean a post polymerisation functionalisation of the end groups that form naturally during the copolymerisation, e.g. to contain curable end groups or end groups that can react with a crosslinker. Crosslinking might also be encouraged through functionalisation of R₁ side groups, such as by pendant functionalisation after polymerisation or by functionalisation of the organic B monomer residue. F and G can be the same or different, typically the same as a slight excess of one of the monomers are used in the polymerisation. Preferably, F and G are alkoxy, such as trialkoxysilane groups such triethoxy or trimethoxy silane groups..

Ideally groups F and G are crosslinking groups, i.e. they are curable with or without the addition of a crosslinking agent. We discuss the option of crosslinking the binder polymer in detail below.

It will be appreciated also that the binder could involve different polysiloxane monomers A' and second and third monomers B'. The possibility of forming a terpolymer and so on is therefore within the scope of the invention.

Copolymer binders may be obtained by mixing all starting materials before polymerisation or by dosing one of the monomers during the reaction. It will be appreciated that the skilled person will know how to carry out polymerisations depending on the monomers employed. The binder which forms is typically an alternating ABABAB polymer of the units used unless the target polymer is a disulphide. It will be appreciated that a polysiloxane unit should preferably not polymerise with itself and the second monomer should preferably not polymerise with itself.

If the target polymer is a disulphide (and hence both monomers carry terminal –SH groups), under the conditions of polymerisation it is possible for monomers to react with themselves. The resulting polymer would be a random copolymer of monomer units.

The polymer is preferably not a block copolymer. If there are two second monomers Ba and Bb then the pattern is preferably AXAXAX where X is randomly

selected from Ba or Bb. The amounts of Ba and Bb present would depend in the stoichiometry of the polymerisation.

The polymerisation conditions can be widely varied although typically temperatures of 20 to 250°C are employed, e.g. 40 to 220°C. In the case that the polymerisation in question is a condensation polymerisation a condensate (normally water or an alcohol) is formed. This is preferably removed by distillation as the polymerisation continues. This can be achieved under reduced pressure. The polymerisation is preferable carried out in an inert atmosphere, e.g. nitrogen or especially under nitrogen stripping conditions. In the case the polymerisation in question is an addition polymerisation, feeding of one of the monomers is preferred due to control of exothermic reaction or to have a control of the molecular design, especially for the endgroups.

The binder of the present invention preferably has a number average molecular weight (M_n) of at least 5,000 g/mol, preferably at least 10,000 g/mol, more preferably at least 15,000 g/mol, especially greater than 20,000 g/mol. In an especially preferred embodiment, values of more than 10,000 g/mol are preferred. The number average molecular weight is preferably up to 100,000 g/mol, such as up to 80,000 g/mol.

There is however, a trade off here as increasing the M_n too far increases viscosity and means that more solvent is required to ensure that the coating composition can be applied. More solvent increases volatile organic content which is not desired. It will be appreciated of course, that the binder as a whole can be made from a mixture of two or more binders with different M_n and/or different hydrolysing properties/rates, i.e. different hydrolysing groups and content of hydrolysing groups. By varying the nature of the binder components, we can vary the speed of hydrolysis.

It is preferred if the binder forms at least 30 wt%, e.g. at least 40 wt%, such as at least 50 wt%, of the coating composition. The binder may form up to 80 wt% or less, such as 70 wt% or less, such as 60 wt% or less of the coating composition.

Crosslinking and curing agent

30

In some embodiments on the invention, it is preferred to crosslink the binder polymer in use. The binder polymer of the invention may possess a curable end group

due to the nature of the groups used to form the binder polymer or due to end capping. Preferably, the end group of the polymer can be end capped with a reactive group to allow a crosslinking reaction to occur. End capping groups of particular interest are trialkoxysilanes.

5 The binder of the invention can be crosslinked in the absence or in the presence of a curing agent.

 Examples of curing agents well known in the art include, for example, monomeric isocyanates, polymeric isocyanates and isocyanate prepolymers. Polyisocyanates are preferred over monomeric isocyanates because of lower toxicity. Polyisocyanates can for example be based on diphenylmethane diisocyanate (MDI),
10 toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) chemistry. These are for example supplied under the tradename Desmodur by Bayer Material Science and Tolonate by Vencorex. Examples of polyisocyanates are Desmodur N3400, Desmodur N3300, Desmodur N3600 Desmodur
15 N75, Desmodur XP2580, Desmodur Z4470, Desmodur XP2565 and Desmodur VL, supplied by Bayer Material Science.

 Polyisocyanates can be made with different NCO-functionality. The NCO-functionality is the amount of NCO-groups per polyisocyanate molecule or isocyanate prepolymer molecule. Polyisocyanates curing agents with different NCO-functionality
20 can be used.

 The curing agent is preferably present in an amount of 0.8-1.5 equivalents (equiv) NCO groups relative the amount of hydroxyl groups, preferably 0.9-1.4 equiv, more preferably 0.95-1.3 equiv, even more preferably 1-1.2 equiv.

 The functionality of the end-groups of the binder will depend on the starting
25 monomers. The end groups can easily be modified to other functional groups suitable for a wide range of curing reactions. Examples of other curable end groups include epoxy groups.

 Ethylenically unsaturated groups such as (meth)acrylate groups may be introduced, for example, by reacting the thiol groups in the binder with ethylenically
30 unsaturated carboxylic acids, such as acrylic acid or methacrylic acid or by using a slight excess of the (meth)acrylate monomer.

It is preferred therefore if the binder inherently contains curable end groups or are modified to contain curable end groups. Compounds which have been modified to contain curable end groups may be referred to specifically as end group modified binders (or end capped modified binders).

5 An alternative end group modifying agent is one comprising an alkoxysilane such as monoalkoxysilane, dialkoxysilane or trialkoxysilane. Current commercial fouling release coatings are commonly cured by a condensation curing mechanism involving hydrolysis of (m)ethoxy-silane compounds. This has advantages compared to e.g. isocyanate-based crosslinking as it minimizes the amount of polar entities
10 introduced (which may cause increased polar interactions with fouling species). In order to facilitate a similar condensation curing mechanism for the binders of the invention, an end-capping reaction of the terminal functional groups may be performed.

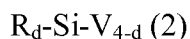
For example, an alkoxysilane such as vinyltrimethoxysilane can be employed to alter a terminal SH group.

15 In a further embodiment therefore, the binder is end capped with a compound comprising the group $-\text{SiR}''_d(\text{OR}')_{3-d}$ where $d=0-2$, R'' and R' independently selected from C_{1-6} alkyl. Examples are trimethoxysilyl, triethoxysilyl, methyldiethoxysilyl, methyldimethoxysilyl, dimethylmethoxysilyl and dimethylethoxysilyl. The compound as a whole comprises this siloxy group and a further functional group capable of
20 reacting with the end group on the formed copolymer binder. The end capping unit is ideally a low molecular weight compound having a M_n of up to 400.

Examples of compounds used include vinyltrimethoxysilane, vinyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 3-aminopropyltri-ethoxysilane, 3-aminopropyltri-
25 methoxysilane and allyltrimethoxysilane. In the presence of moisture, the siloxy end groups present at the end of the binder will then begin to crosslink. In some instances the end groups may be mono(m)ethoxysilane in which case a separate crosslinking agent may be used to cure the coating (e.g. alkoxysilane such as tetraethoxysilane or condensation products thereof (e.g. WACKER® TES 40 WN)).

30 The cross-linking agent preferably constitutes 0-10 % by dry weight of the coating composition and is, e.g. an organosilicon compound represented by the general

formula (2) shown below, a partial hydrolysis-condensation product thereof, or a mixture of the two:



5

wherein, each R represents, independently, an unsubstituted or substituted monovalent hydrocarbon group of 1 to 6 carbon atoms, each V represents, independently, a hydrolysable group, and d represents an integer from 0 to 2, such as from 0 to 1.

10

The mixing of the binder polymer and the curing agent can be carried out shortly before application of the coating to an object, e.g. an hour or less before coating or the binder can be supplied in curable form but kept dry in order to prevent premature curing. In some embodiments the curing agent/end capping agent is supplied separately to the rest of the coating composition to prevent curing before the coating has been applied to the object. In case the ends are mono(m)ethoxysilane a (m)ethoxysilane crosslinker, e.g. TES 40 WN, may be used in combination with the binder. Hence the coating composition of the invention can be supplied as a multipack (preferably two pack) formulation.

15

20

Viewed from another aspect therefore the invention provides a kit comprising (I) a binder polymer as described herein and (II) a curing. It would preferably be supplied with instructions on mixing the components shortly before application. One or other component may also be supplied with a catalyst to encourage the crosslinking process.

25

Coating Composition

The coating composition of the invention contains the binder or a mixture of binders. The composition may also contain other conventional components of a fouling release composition.

30

The polysiloxane-based binder system typically constitutes 20-90% by dry weight, at least 40% by dry weight, in particular 50-90% by dry weight, of the coating composition.

The binder of the present invention will degrade in sea water. It will be understood that the degradation reactions which the binder undergoes is a hydrolysis reaction which occurs in the polymer backbone, i.e. the hydrolysable bonds are present in the polymer backbone.

5 In addition to the binder, the coating composition of the invention may include other components such as additive oils, catalysts, biocides, enzymes and cobinders. Other conventional components include solvents, additives, pigments and fillers.

Additive oils

10 The coating composition might contain well known hydrophilic-modified additive oils e.g. as described in WO2011/076856. The composition may further include hydrophilic-modified polysiloxane oils, i.e. constituents which do not form covalent bonds to the estersiloxane-based binder matrix. Hydrophilic- modified polysiloxane oils are widely used as surfactants and emulsifiers due to the content of
15 both hydrophilic and lipophilic groups in the same molecule. In contrast to the estersiloxane components discussed above, the hydrophilic-modified polysiloxane oils are selected so that they do not contain groups that can react with the binder (or binder components) or the cross-linker (if present), hence the hydrophilic-modified polysiloxane oils are intended to be non-reactive, in particular with respect to the binder
20 components. In particular, the hydrophilic-modified polysiloxane oils are devoid of any silicon-reactive groups such as Si-OH groups, hydrolysable groups such as Si-OR (such as alkoxy, oxime, acetoxy etc.) groups, so as to avoid reaction with constituents of the estersiloxane-based binder system.

The non-reactive hydrophilic-modified polysiloxane oils are typically modified
25 by the addition of non-ionic oligomeric or polymeric groups which can be polar and/or capable of hydrogen bonding, enhancing their interaction with polar solvents, in particular with water, or with other polar oligomeric or polymeric groups. Examples of these groups include, amides (e.g. poly(vinyl pyrrolidone), poly[N-(2-hydroxypropyl)methacrylamide]), poly(N,N- dimethacrylamide), acids (e.g. poly(acrylic acid)), alcohols (e.g. poly(glycerol), polyHEMA, polysaccharides,
30 poly(vinyl alcohol)), ketones (polyketones), aldehydes (e.g. poly(aldehyde guluronate), amines (e.g. polyvinylamine), esters (e.g. polycaprolactones, poly(vinyl acetate)),

ethers (e.g. polyoxyalkylenes like poly(ethylene glycol), poly(propylene glycol)), imides (e.g. poly(2-methyl-2-oxazoline)), etc., including copolymers of the foregoing.

Preferably the hydrophilicity is obtained by modification with polyoxyalkylene groups. In a preferred embodiment, the hydrophilic-modified polysiloxane oil (if
5 present) has a number average molecular weight (M_n) in the range of 100-100,000 g/mol, such as in the range of 250-75,000 g/mol, in particular in the range of 500-50,000 g/mol.

The one or more hydrophilic-modified polysiloxane oils are included in the coating composition in an amount of 0.01-30 %, e.g. 0.05-10 %, by dry weight. In
10 certain embodiments, the one or more hydrophilic-modified polysiloxane oils constitutes 0.05-7 % by dry weight, e.g. 0.1-5 % by dry weight, in particular 0.5-3 % by dry weight, of the coating composition.

Other additive oils of interest are described in WO2008132196. Suitable unreactive fluids are silicone oils such as methylphenyl silicone oil,
15 polydimethylsiloxane, carboxyl-functional organosiloxanes as disclosed in WO 2008/132195; petroleum oils, polyolefin oils, polyaromatic oils, fluoro resins such as polytetra- fluoroethylene or fluid fluorinated alkyl- or alkoxy-containing polymers, or lanolin and lanolin derivatives and other sterol(s) and/or sterol derivative(s) as disclosed in PCT Application No PCT/EP2012/065920 or combinations thereof. A
20 preferred unreactive fluid is methylphenyl silicone oil. Also of interest are fluorinated amphiphilic polymers/oligomers described in WO2014131695. The proportion of unreacted fluid is preferably 5-25 wt%, more preferably 5-10 wt%, based on the solids content of the coating composition.

25 **Biocides/ Marine Anti-fouling agent**

In one embodiment, a biocide can be used in the binder of the invention. Suitable biocides are well known and can be found in WO2013/000479.

In the present context, the term "biocide" is intended to mean an active
30 substance intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful marine organism by chemical or biological means. Illustrative examples of biocides are those selected from metallo-

dithiocarbamates such as bis(dimethyldithiocarbamato)zinc, ethylene-
 bis(dithiocarbamato)zinc, ethylene-bis(dithio-carbamato)manganese, and complexes
 between these; bis(1-hydroxy-2(1H)-pyridine- thionato-0,S)-copper; copper acrylate;
 bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-zinc; phenyl(bispyridyl)-bismuth dichloride;
 5 metal biocides such as copper(I)oxide, cuprous oxide, metallic copper, copper metal
 alloys such as copper-nickel alloys; metal salts such as cuprous thiocyanate, basic
 copper carbonate, copper hydroxide, barium metaborate, and copper sulphide;
 heterocyclic nitrogen compounds such as 3a,4,7,7a-tetrahydro-2-((trichloro- methyl)-
 thio)-1H-isoindole-1,3(2H)-dione, pyridine-triphenylborane, 1-(2,4,6-trichloro- phenyl)-
 10 1H-pyrrole-2,5-dione, 2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine, 2-methylthio- 4-
 tert-butylamino-6-cyclopropylamine-s-triazin, and quinoline derivatives; heterocyclic
 sulfur compounds such as 2-(4-thiazolyl)benzimidazole, 4,5-dichloro-2-n-octyl-4-
 isothiazolin-3-one, 4,5-dichloro-2-octyl-3(2H)-isothiazoline (Sea-Nine®-211N), 1,2-
 benzisothiazolin-3-one, and 2-(thiocyanatomethylthio)-benzothiazole; urea derivatives
 15 such as N-(1,3- bis(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl)-N,N'-
 bis(hydroxymethyl)urea, and N-(3,4- dichlorophenyl)-N,N-dimethylurea, N,N-
 dimethylchlorophenylurea; amides or imides of carboxylic acids; sulfonic acids and of
 sulfenic acids such as 2,4,6-trichlorophenyl maleimide, 1.1- dichloro-N-
 ((dimethylamino)sulfonyl)-1-fluoro-N-(4-methylphenyl)-methanesulfenamide, 2.2-
 20 dibromo-3-nitrilo-propionamide, N-(fluorodichloromethylthio)-phthalimide, N,N-
 dimethyl- N'-phenyl-N'-(fluorodichloromethylthio)-sulfamide, and N-methylol
 formamide; salts or esters of carboxylic acids such as 2-((3-iodo-2-propynyl)oxy)-
 ethanol phenylcarbamate and N,N- didecyl-N-methyl-poly(oxyethyl)ammonium
 propionate; amines such as dehydroabiethyl- amines and cocodimethylamine;
 25 substituted methane such as di(2-hydroxy-ethoxy)methane, 5,5'-dichloro-2,2'-
 dihydroxydiphenylmethane, and methylene-bisthiocyanate; substituted benzene such as
 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile, 1,1-dichloro-N-((dimethyl- amino)-
 sulfonyl)-1-fluoro-N-phenylmethanesulfenamide, and 1-((diiodomethyl)sulfonyl)-4-
 methyl-benzene; tetraalkyl phosphonium halogenides such as tri-n-butyltetradecyl
 30 phosphonium chloride; guanidine derivatives such as n-dodecylguanidine
 hydrochloride; disulfides such as bis-(dimethylthiocarbamoyl)-disulfide,
 tetramethylthiuram disulfide; phenylcapsaicin;

imidazole containing compound, such as medetomidine; 2-(p-chlorophenyl)-3-cyano-4-bromo-5-trifluoromethyl pyrrole and mixtures thereof. Presently, it is preferred that the biocide does not comprise tin.

Currently preferred biocides are those selected from the group consisting of

5 2,4,5,6-tetra-chloroisophthalonitrile (Chlorothalonil), copper thiocyanate (cuprous sulfocyanate), N-dichloro-fluoromethylthio-N',N'-dimethyl-N-phenylsulfamide (Dichlofluanid), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (Diuron), N2-tert-butyl-N4-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine (Cybutryne), 4-bromo-2-(4-chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, (2-(p-chlorophenyl)-3-

10 cyano-4-bromo-5-trifluoromethyl pyrrole; Tralopyril), Cybutryne, (RS)-4-[1-(2,3-dimethylphenyl)ethyl]-3H-imidazole (Medetomidine), 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine® 211N), dichlor-N-((dimethylamino)sulfonyl)fluor-N-(p-tolyl)methanesulfenamid (Tolylfluanid), 2-(thiocyanomethylthio)-1,3-benzothiazole ((2-benzothiazolylthio)methyl thiocyanate;

15 TCMTB), triphenylborane pyridine (TPBP); bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-(T-4) zinc (zinc pyridinethione; zinc pyrithione), bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-T-4) copper (copper pyridinethione; copper pyrithione; Copper Omadine), zinc ethylene-1,2-bis-dithiocarbamate (zinc-ethylene-N,N'-dithiocarbamate; Zineb), copper(I) oxide, metallic copper, 3-(3,4-dichlorophenyl)-1,1-dimethylurea

20 (Diuron) and diiodomethyl-p-tolylsulfone; phenylcapsaicin. Preferably at least one biocide is selected from the above list.

In a particularly preferred embodiment, the biocides are preferably selected among biocides which are effective against soft fouling such as slime and algae. Examples of such biocides are N2-tert-butyl-N4-cyclopropyl-6-methylthio-1,3,5-

25 triazine-2,4-diamine (Cybutryne), 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine® 211N), bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-(T-4) zinc (zinc pyridinethione; zinc pyrithione), bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-T-4) copper (copper pyridinethione; copper pyrithione) and zinc ethylene-1,2-bis-

30 dithiocarbamate (zinc-ethylene-N,N'-dithiocarbamate; Zineb), bis(1-hydroxy-2(1H)-pyridinethionato-0,S)-T-4) copper (copper pyridinethione; copper pyrithione; Copper Omadine). For hard fouling, copper(I) oxide, metallic copper, copper thiocyanate, (cuprous sulfocyanate) may be used.

In a further particularly preferred embodiment, the biocide is an organic biocide, such as a pyrrithione complex, such as zinc pyrrithione, or such as copper pyrrithione. Organic biocides are those either fully or in part being of organic origin. Optionally the marine anti-fouling agents may be encapsulated or adsorbed on an inert carrier or
 5 bonded to other materials for controlled release.

The total amount of organic biocide in the antifouling compositions of the invention may be in the range 0.1 to 40 wt%, such as 0.1 to 20 wt%, such as 0,5 to 10 wt% (dry weight of the coating composition), e.g. 1-8 wt%. The total amount of inorganic biocides such as cuprous oxide, copper (I) oxide, metallic copper etc. in the
 10 antifouling composition of the invention may be in the range of 0,5-80% by dry weight, such as 1-70%. It will be appreciated that the amount of this component will vary depending on the end use and the marine anti-fouling agent used.

Catalyst

15

In order to assist the curing process, the coating composition of the invention might contain a catalyst. WO2014/131695 gives an extensive list of possible catalysts. Examples of catalysts that can be used include transition metal compounds, metal salts and organometallic complexes of various metals, such as tin, iron, lead, barium, cobalt,
 20 zinc, antimony, cadmium, manganese, chromium, nickel, aluminium, gallium, germanium and zirconium. The salts preferably are salts of long-chain carboxylic acids and/or chelates or organometal salts. Examples of suitable catalysts include for example, dibutyltin dilaurate, dibutyltin dioctoate, dibutyl tin diacetate, dibutyl tin 2-ethylhexanoate, dibutyltin di neodecanoate, dibutyl tin dimethoxide, dibutyltin
 25 dibenzoate, dibutyltin acetoacetate, dibutyltin acetylacetate, dibutyltin alkylacetoacetate, dioctyltin dilaurate, dioctyltin dioctoate, dioctyl tin diacetate, dioctyl tin 2-ethylhexanoate, dioctyltin di neodecanoate, dioctyl tin dimethoxide, dioctyltin dibenzoate, dioctyltin acetoacetate, dioctyltin acetylacetate, dioctyltin alkylacetoacetate, dimethyltin dibutyrate, dimethyltin bisneodecanoate, dimethyltin
 30 dineodecanoate, tin naphthenate, tin butyrate, tin oleate, tin caprylate, tin octanoate, tin stearate, tin octoate, iron stearate, iron 2-ethylhexanoate, lead octoate, lead 2-ethyloctoate, cobalt-2-ethylhexanoate, cobalt naphthenate, manganese 2-

ethylhexanoate, zinc 2-ethylhexanoate, zinc naphthenate, zinc stearate, metal triflates, triethyl tin tartrate, stannous octoate, carbomethoxyphenyl tin trisuberate, isobutyl tin triceroate.

Further examples of suitable catalysts include organobismuth compounds, such as bismuth 2-ethylhexanoate, bismuth octanoate and bismuth neodecanoate. Further examples of suitable catalysts include organotitanium, organozirconium and organohafnium compounds and titanates and zirconate esters such as, titanium naphthenate, zirconium naphthenate, tetrabutyl titanate, tetrakis(2-ethylhexyl)titanate, triethanolamine titanate, tetra(isopropenyloxy)-titanate, titanium tetrabutanolate, titanium tetrapropanolate, titanium tetraisopropanolate, tetrabutyl zirconate, tetrakis(2-ethylhexyl) zirconate, triethanolamine zirconate, tetra(isopropenyloxy)-zirconate, zirconium tetrabutanolate, zirconium tetrapropanolate, zirconium tetraisopropanolate and chelated titanates such as diisopropyl bis(acetylacetonate)titanate, diisopropyl bis(ethylacetoacetate)titanate and diisopropoxytitanium bis(ethylacetoacetate), and the like.

Preferably the catalyst is present in an amount of 0.01 to 5wt% based on the total weight of the coating composition, especially 0.05 to 4 wt%.

Solvent, Pigments, Fillers and Additives

The coating may contain solvents. Suitable solvents include aliphatic, cycloaliphatic and aromatic hydrocarbons, alcohols, ketones, esters, and mixtures of the above. Examples of suitable solvents are white spirit, cyclohexane, toluene, xylene and naphtha solvent, esters such as methoxypropylacetate, n-butyl acetate and 2-ethoxyethylacetate; octamethyltrisiloxane, and mixtures thereof. The solvents, if any, typically constitute 5 to 50 wt% based on the total weight of the coating composition. The solid content may be determined in accordance with ASTM method D2697.

The coating composition of the invention may also comprise pigments. Examples of pigments include black iron oxide, red iron oxide, yellow iron oxide, titanium dioxide, zinc oxide, carbon black, graphite, red molybdate, yellow molybdate, zinc sulfide, antimony oxide, sodium aluminum sulfosilicates, quinacridones, phthalocyanine blue, phthalocyanine green, indanthrone blue, cobalt aluminium oxide,

carbazoledioxazine, chromium oxide, isoindoline orange, bis-acetoaceto-tolidiole, benzimidazolone, quinaphthalone yellow, isoindoline yellow, tetrachloroisoindolinone, and quinophthalone yellow, metallic flake materials (e.g. aluminium flakes) or other so-called barrier pigments or anticorrosive pigments such as zinc dust or zinc alloys or other so-called lubricant pigments such as graphite, molybdenum disulfide, tungsten disulphide or boron nitride. Preferred pigments are black iron oxide, red iron oxide, yellow iron oxide, sodium aluminium sulfosilicate and titanium dioxide.

The proportion of pigment may be in the range of from 0 to 25 wt% by weight, based on the total weight of the coating composition, preferably in the range 0 to 15 wt%.

The coating composition of the invention may also comprise fillers. Examples of fillers that can be used in the coating composition according to the present invention are zinc oxide, barium sulphate, calcium sulphate, calcium carbonate, silicas or silicates (such as talc, feldspar, and china clay) including pyrogenic silica, bentonite and other clays, and solid silicone resins, which are generally condensed branched polysiloxanes. Some fillers such as fumed silica may have a thixotropic effect on the coating composition. The proportion of fillers may be in the range of from 0 to 25 wt% by weight, based on the total weight of the coating composition, preferably in the range 0 to 10 wt% and more preferably in the range 0 to 5 wt%.

The coating composition according to the present invention optionally comprises one or more components selected among other surfactants, wetting agents, thickeners, antissettling agents, and dyes.

An additional binder can be used to adjust the self-polishing properties and the mechanical properties of the coating film. Examples of binders that can be used in addition to the binder of the invention in the coating composition according to the present invention include other polysiloxanes.

Application of the coating composition

The coating composition of the invention can be applied to a whole or part of any object surface which is subject to fouling. The surface may be permanently or intermittently underwater (e.g. through tide movement, different cargo loading or swell). The object surface will typically be the hull of a vessel or surface of a fixed

marine object such as an oil platform or buoy. Application of the coating composition can be accomplished by any convenient means, e.g. via painting (e.g. with brush or roller) or spraying the coating onto the object. Typically the surface will need to be separated from the seawater to allow coating. The application of the coating can be achieved as conventionally known in the art.

The coating composition can be applied by normal techniques, such as brushing, roller coating, or spraying (airless and air-assisted). To achieve proper adhesion to the substrate it is preferred to apply the coating composition to a primed substrate. The primer can be any conventional primer/sealer coating system suitable for PDMS coating. It is also possible to apply the coating composition according to the present invention on a substrate containing an aged anti-fouling coating layer or fouling release layer. Before the coating composition according to the present invention is applied to such an aged layer, this old layer is cleaned by high-pressure water washing to remove any fouling. The primer disclosed in WO 99/33927 can be used as a tie coat between the aged coating layer and the coating composition according to the present invention. Optionally the primer may comprise adhesion promoters as disclosed in WO 2010/018164.

Optionally the primer may comprise a biocide. After the coating has been cured it can be immersed immediately and gives immediate anti-fouling or fouling-release protection. As indicated above, the coating composition according to the present invention has very good anti-fouling and fouling-release properties. This makes these coating compositions very suitable for use as anti-fouling or fouling release coatings for marine applications. The coating can be used for both dynamic and static structures, such as boat hulls, buoys, drilling platforms, dry dock equipment, oil and/or gas production rigs, floating oil and gas processing, storage and offloading vessels, aqua culture equipment, netting and cages, energy generation devices such as offshore wind turbines and tidal and wave energy devices, cooling water intakes for power plants and power stations and pipes which are immersed in water and tanks, pipes and conduits used to store and transport water. The coating can be applied on any substrate that is used for these structures, such as metal, concrete, wood, plastic or fibre-reinforced plastic.

The invention will now be defined with reference to the following non limiting examples.

Determination of polymer molar mass distribution

5 The polymers are characterised by Gel Permeation Chromatography (GPC) measurement. Instrument details are:

a. Tetrahydrofuran as mobile phase:

10 The molecular weight distribution (MWD) was determined using a Polymer Laboratories PL-GPC 50 instrument with two PLgel 5 μ m Mixed-D columns (300 x 7.5 mm) from Polymer Laboratories in series, Tetrahydrofuran as an eluent at ambient temperature and at a constant flow rate of 1 mL/min and with a refractive index (RI) detector. The columns were calibrated using polystyrene standards Easivials PS-M from Polymer Laboratories. The data were processed using Cirrus software from Polymer Labs.

15 b. Toluene as mobile phase:

The molecular weight distribution (MWD) was determined using a EcoSEC instrument with Micro SDV columns (1000/10000 Å, 55 cm length and 0.4 cm ID) from Tosoh Bioscience GmbH. Toluene used as an eluent at 35 °C temperature and at a constant flow rate of 0.35 mL/min and with a refractive index (RI) detector. The
20 columns were calibrated using polystyrene standards (162-2,520,000 g/mol) from PSS.

Samples were prepared by dissolving an amount of polymer solution corresponding to 5 mg dry polymer in 5 mL Tetrahydrofuran or Toluene. The samples were kept for minimum 4 hours at room temperature prior to sampling for the GPC
25 measurements.

The weight-average molecular weight (M_w), the number-average molecular weight (M_n) and the dispersity (D_M), equivalent to M_w/M_n , are reported.

Chemicals:

30 Alpha,omega amino siloxane [Tegomer A-Si 2122 (n=10) or Tegomer A-Si 2322 (n=30)], Bis[3-(trimethoxysilyl)propyl]amine (Dynasylan® 1124), alpha, omega hydroxy alkyl siloxane (Tegomer® H-Si 2515), available from Evonik

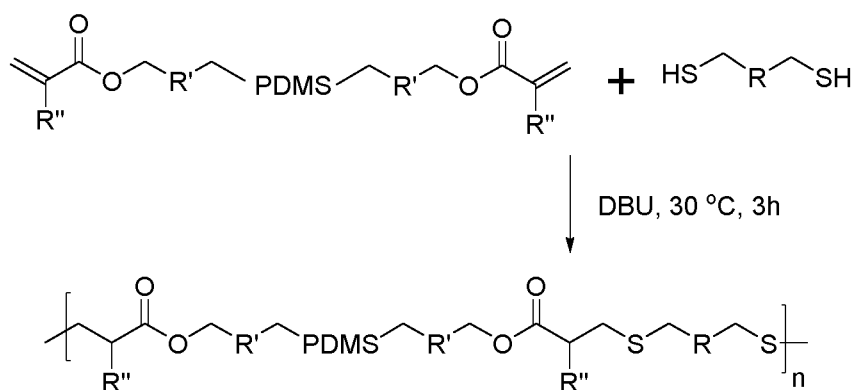
Methyl 5-Hexenoate, Nonanediol diacrylate, available from TCI Europe GmbH)Ti(IV) Butoxide, Dibutyltin dilaurate, 1,8-diaza-7-bicyclo[5.4.0]undecene (DBU), Dimethyltindichloride, p-Toluenesulphonic acid, available from Sigma-Aldrich.

- 5 Methacryloxypropyl terminated polydimethyl siloxane monomers, Vinyl terminated polydimethylsiloxane, (3-Mercaptopropyl) trimethoxysilane, Acryloxy terminated ethyleneoxide-dimethylsiloxane-ethyleneoxide available from ABCR Chemicals. (Mercaptopropyl)methyl terminated siloxane available from GP silicones.
- 10 1,8-Octanedithiol, Succinic anhydride, Allyl alcohol, Benzoquinone, 2,2'-Azobis(2-methylpropionitrile), Triethylamine, Succinic acid, 2-Mercaptoethanol, Diethylene glycol monoallyl ether, Hexamethylenediamine, Dimethylsuccinate, 2-(Methylamino)ethanol, anhydrous xylene, anhydrous methylene dichloride, anhydrous dioxane, available from Sigma-Aldrich.

15

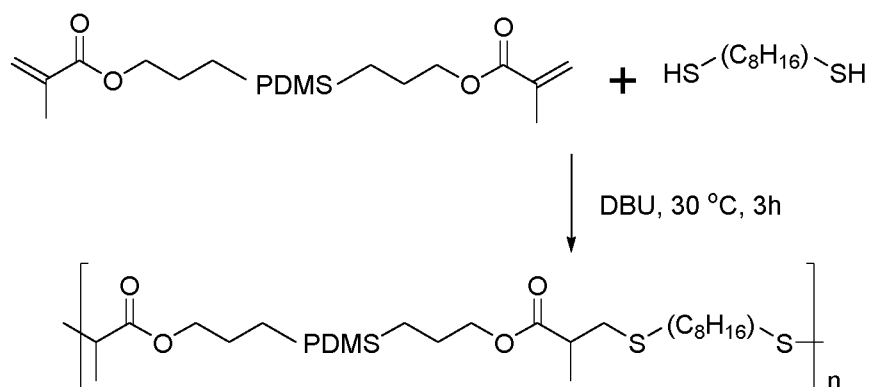
Examples

Example 1a: Thiol-ene Michael addition reaction: General scheme



$\text{R}'' = \text{H or CH}_3$

- 20 In a multi-neck flask with nitrogen line, stirring device and internal thermometer, methacryloxypropyl terminated polydimethylsiloxane (DMS-R18, CAS No. 58130-03-3, ABCR Chemicals) (100g, 0.04 eq.mol), 1,8 Octanedithiol (14.58g, 0.04 eq.mol) and 1,8-diaza-7-bicyclo[5.4.0]undecene (DBU) (0.115g, 0.1 wt%) were dissolved in anhydrous xylene:



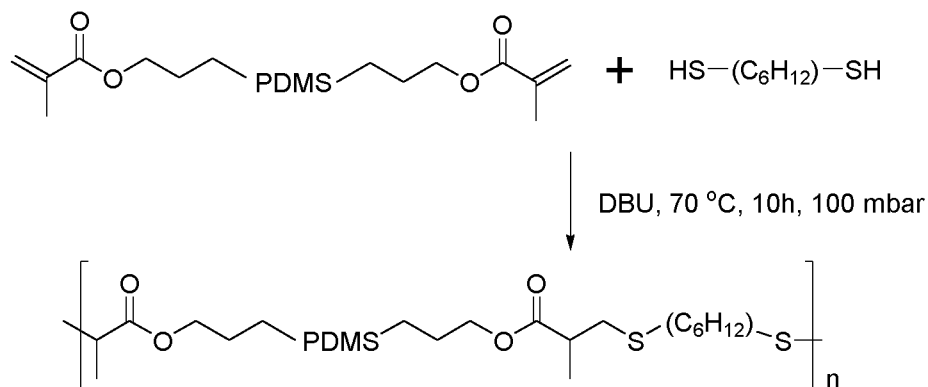
- 5 The mixture was stirred at 30 °C for 3h under nitrogen atmosphere. Xylene and all volatiles were removed by vacuum distillation (3h, 80 °C, <1 mbar).

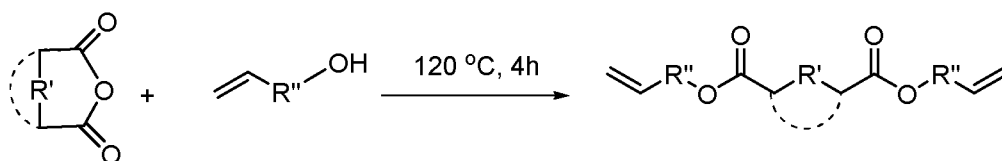
GPC data: M_w 9246 g/mol, M_n 4020 g/mol, MWD 2.3 (Toluene, PS standards, 35°C)

Example 1b:

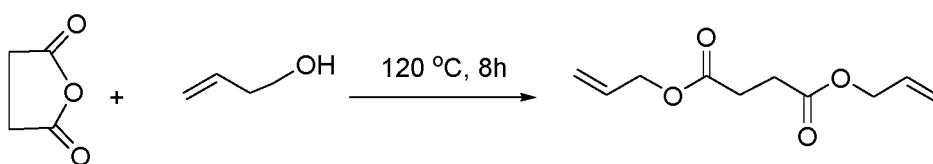
- 10 In a multi-neck flask with nitrogen line, stirring device and internal thermometer, methacryloxypropyl terminated polydimethylsiloxane (DMS-R18, CAS No. 58130-03-3, ABCR Chemicals) (150g, 0.01182 mol, vinyl), 1,6 Hexanedithiol (2.49g, 0.016.mol) and 1,8-diaza-7-bicyclo[5.4.0]undecene (DBU) (0.15g, 0.1 wt%) were mixed. Reaction mixture was stirred at 70 °C for 10h under vacuum (100 mbar).

- 15 GPC data: M_w 11264 g/mol, M_n 5587 g/mol, MWD 2.02 (Toluene, PS standards, 35°C)

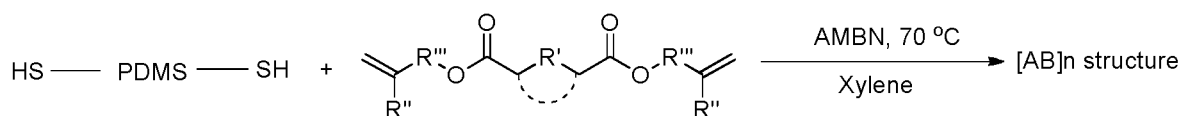


Example 2a5 **Synthesis of functionalized di-esters: General scheme**

In a multi-neck flask with nitrogen line, stirring device and internal thermometer,
 Succinic anhydride (50g, 0.5 mol), Allyl alcohol (87g, 1.5 mol), benzoquinone (0.05g)
 10 and Titanium (IV) butoxide (0.1 g) were dissolved in anhydrous xylene:



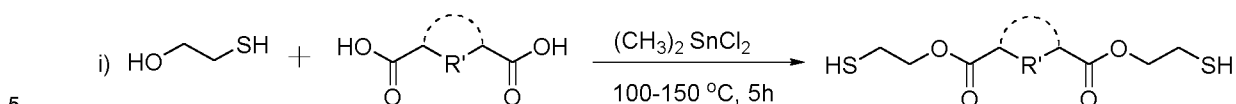
The mixture was stirred at 120 °C for 8h under smooth nitrogen atmosphere stripping
 conditions. Xylene and residual alcohol were removed by vacuum distillation (3h, 80
 °C, 10 mbar).

15 **Example 2b**

In a multi-neck flask with nitrogen line, stirring device and internal thermometer, a,w-
 (mercaptopropyl) dimethylsiloxane (100g, 0.026 mol-SH functionality),
 20 diallylsuccinate (12.29, 0.062 mol) and 2,2'-Azobis(2-methylpropionitrile) (100 mg)
 were dissolved in anhydrous xylene. The mixture was stirred at 70 °C for 5h under

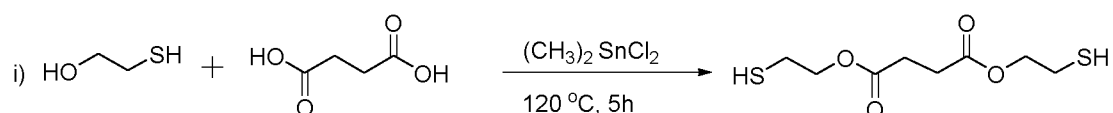
nitrogen atmosphere. Xylene and residual volatiles were removed by vacuum distillation (3h, 80 °C, 10 mbar)

Example 3a Siloxane-ene + Thiol terminated ester General Scheme



In a multi-neck flask with nitrogen line, stirring device and internal thermometer, succinic acid (100g, 0.931 mol), 2-Mercaptoethanol (77.27 g, 1 mol) and dimethyltin dichloride (0.05 wt%) were dissolved in anhydrous xylene:

10



The mixture was stirred at 120 °C for 5h under nitrogen. Xylene was removed by vacuum distillation at 120 °C <50 mbar.

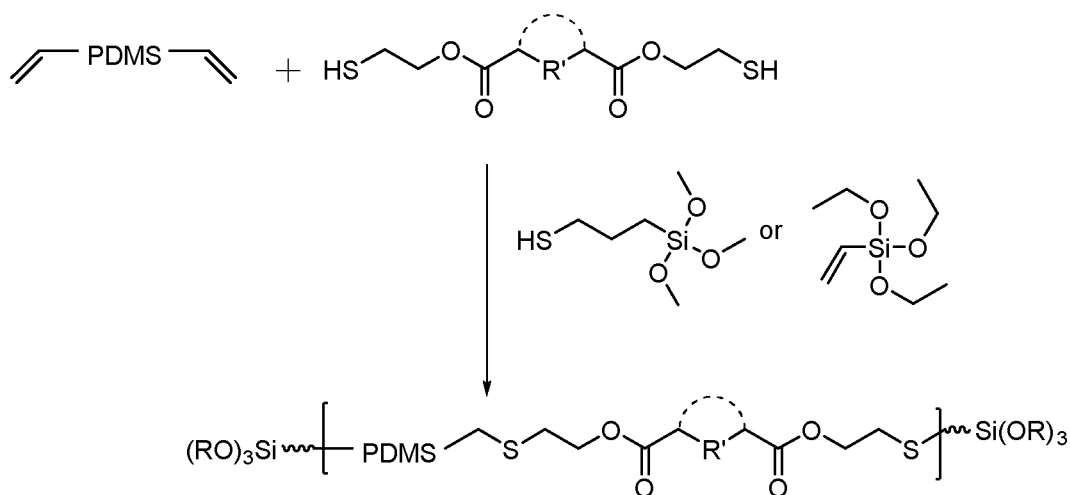
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Example 3b - one pot synthesis

In a multi-neck flask with nitrogen line, stirring device and internal thermometer, vinyl terminated polydimethylsiloxane (DMS-V03, CAS. 68083-19-2, ABCR Chemicals) (100g, 0.0133 mol), Bis(2-mercaptoethyl)succinate (3.35g, 0.0133 mol), (3-Mercaptopropyl)trimethoxysilane (0.19g, 0.001 mol) and 2,2'-Azobis(2-methylpropionitrile) (100 mg) were dissolved in anhydrous xylene. The mixture was stirred at 70 °C for 3h under nitrogen atmosphere. Xylene was removed by vacuum distillation (3h, 80 °C, <1 mbar).

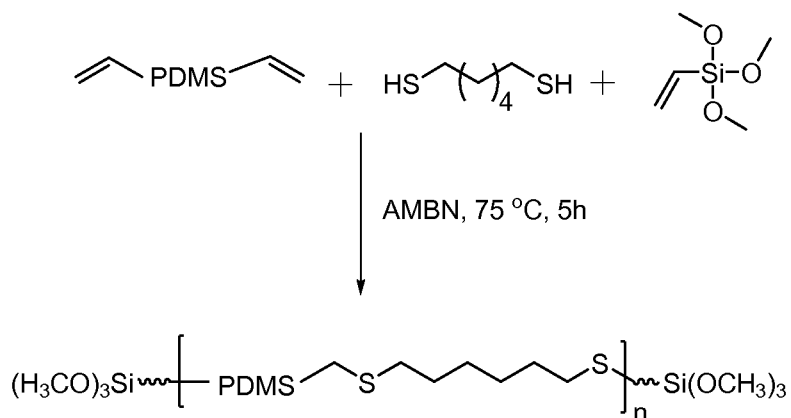
20

GPC data: M_w 23565 g/mol, M_n 7601 g/mol, MWD 3.1(Toluene, PS standards, 35°C)

**Example 3c.**

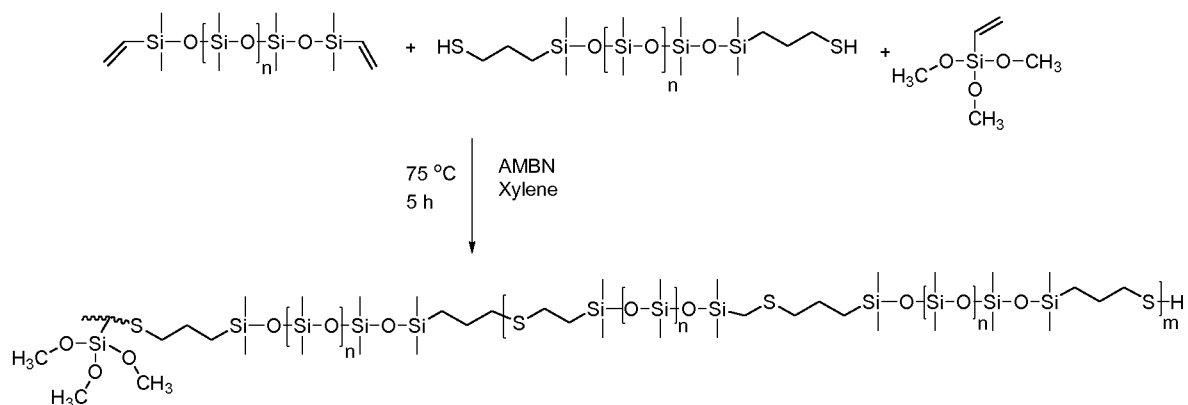
In a multi-neck flask equipped with nitrogen line, stirring device and internal thermometer. 50 mL of anhydrous xylene was added to the flask. Xylene temperature was maintained at 75 °C under nitrogen atmosphere. In a dropping funnel α,ω -vinyl terminated polydimethylsiloxane (CAS. 68083-19-2, ABCR Chemicals) (100g, 0.04 mol), 1,6 Hexanedithiol 6g, 0.04 mol), vinyltrimethoxysilane (1.48g, 0.01 mol) were mixed. In another dropping funnel 2,2-Azodi(2-methylbutyronitril) (AMBN) (500 mg) are dissolved in 10 mL anhydrous xylene. Reaction mixture and initiator solution were added dropwise to xylene solution at 75 °C for 2h. The mixture was stirred at 75 °C for another 3h under nitrogen atmosphere. Later xylene was removed by vacuum distillation (3h, 80 °C, <1 mbar).

GPC data: M_w 29056 g/mol, M_n 8726 g/mol, MWD 3.33 (Toluene, PS standards, 35°C)

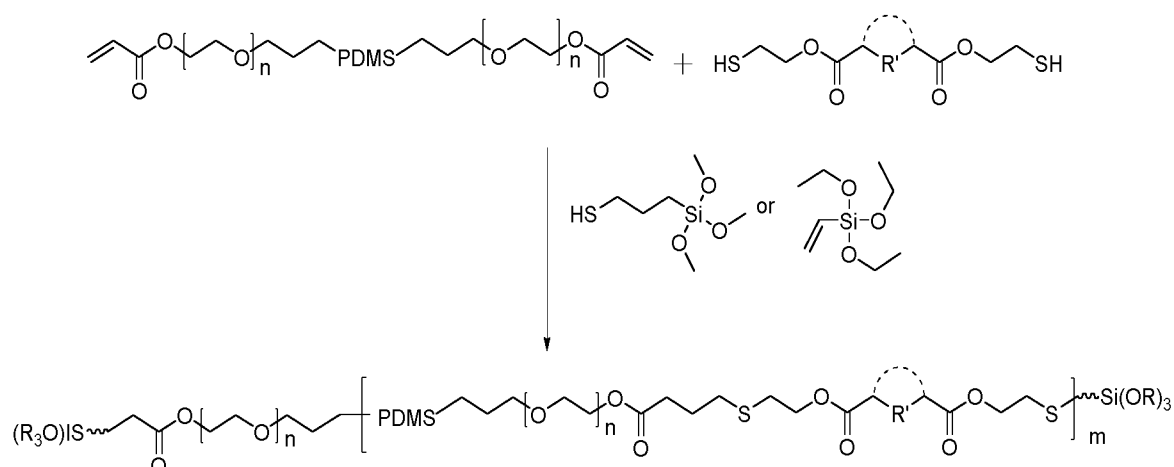
**Example 3d:**

In a multi-neck flask equipped with nitrogen line, stirring device and internal thermometer. 50 mL of anhydrous xylene was added to the flask. Xylene temperature was maintained at 75 °C under nitrogen atmosphere. In a dropping funnel α,ω -vinyl terminated polydimethylsiloxane (CAS. 68083-19-2, ABCR Chemicals) (65g, 0.026 mol), α,ω -(mercaptopropyl) dimethylsiloxane (GP silicones 100g, 0.026 mol, -SH functionality), vinyltrimethoxysilane (1.92g, 0.013 mol) were mixed. In another dropping funnel 2,2-Azodi(2-methylbutyronitril) (AMBN) (500 mg) are dissolved in 10 mL anhydrous xylene. Reaction mixture and initiator solution were added dropwise to xylene solution at 75 °C for 2h. The mixture was stirred at 75 °C for another 3h under nitrogen atmosphere. Later xylene was removed by vacuum distillation (3h, 80 °C, <1 mbar)

GPC data: M_w 36,029 g/mole, M_n 10,722 g/mole, MWD 3.36 (Toluene, PS standards, 35°C)



Example 4 – General Scheme



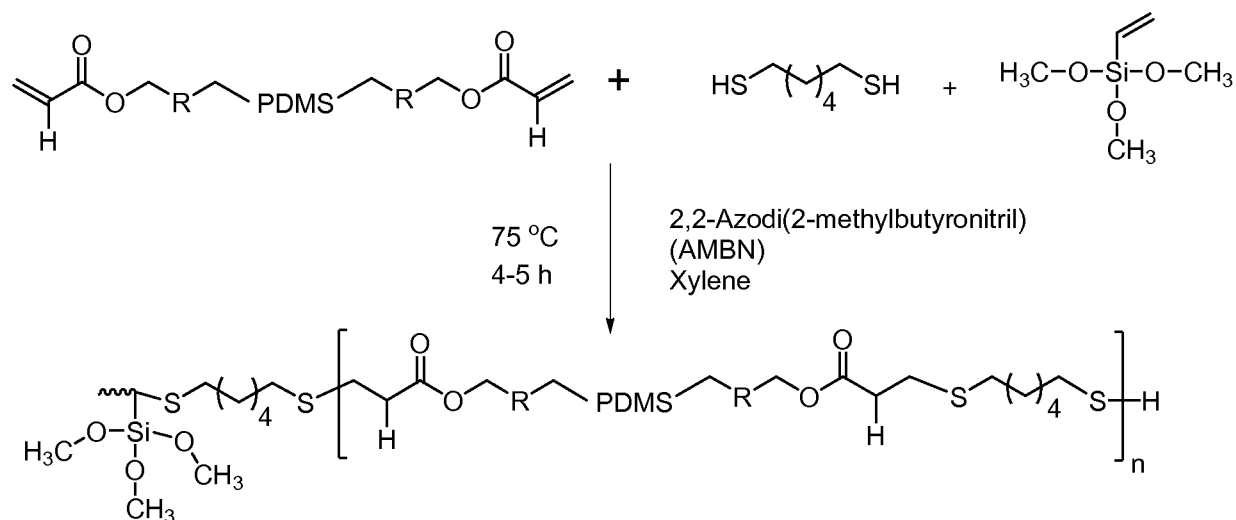
Example 4a

In a multi-neck flask with nitrogen line, stirring device and internal thermometer,
 5 acryloxy terminated ethyleneoxide-dimethylsiloxane-ethyleneoxide (ABA block
 copolymer) (DBE-U22, CAS. 117440-21-9, ABCR Chemicals) (100g, 0.058.mol),
 bis(2-mercaptoethyl) succinate (14.01g, 0.058 mol), (3-
 Mercaptopropyl)trimethoxysilane (1.12g, 0.006 mol) and 1,8-diaza-7-
 bicyclo[5.4.0]undecene (DBU) (0.126g, 0. 1 wt%) were dissolved in anhydrous xylene.
 10 The mixture was stirred at 40 °C for 3h under nitrogen atmosphere. Xylene was
 removed by vacuum distillation (3h, 80 °C, <1 mbar).

GPC data: M_w 20987 g/mol, M_n 7442 g/mol, MWD 2.82 (Toluene, PS standards, 35°C)

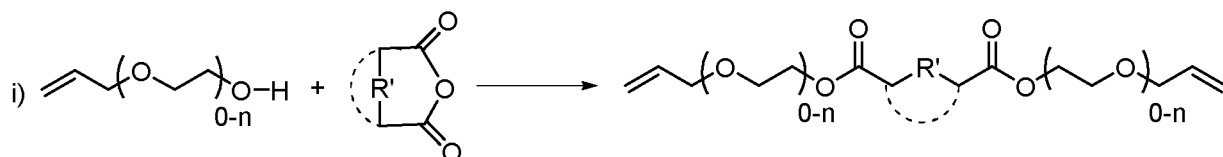
Example 4b:

In a multi-neck flask equipped with nitrogen line, stirring device and internal
 15 thermometer. 50 mL of anhydrous xylene was added to the flask. Xylene temperature
 was maintained at 75 °C under nitrogen atmosphere. In a dropping funnel acryloxy
 terminated ethyleneoxide-dimethylsiloxane-ethyleneoxide (ABA block copolymer)
 (DBE-U22, CAS. 117440-21-9, ABCR Chemicals) (100g, 0.058.mol), 1,6
 Hexanedithiol (8.72g, 0.058 mol), vinyltrimethoxysilane (4.29g, 0.029 mol) were
 20 mixed. In another dropping funnel 2,2-Azodi(2-methylbutyronitril) (AMBN) (500 mg)
 are dissolved in 10 mL anhydrous xylene. Reaction mixture and initiator solution were
 added dropwise to xylene solution at 75 °C for 2h. The mixture was stirred at 75 °C for
 another 3h under nitrogen atmosphere.

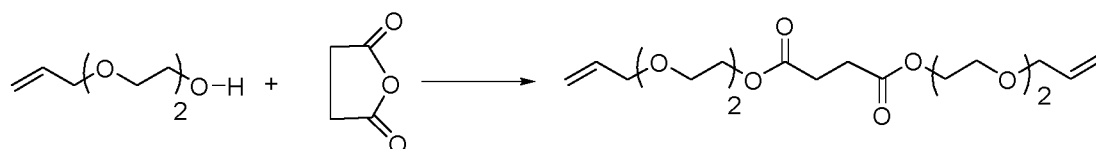


GPC data: M_w 40,524 g/mol, M_n 6,484 g/mol, MWD 6.25 (THF, PS standards, 35°C)

5 Example 5a Siloxane-thiol + Allyl terminated diester General Scheme

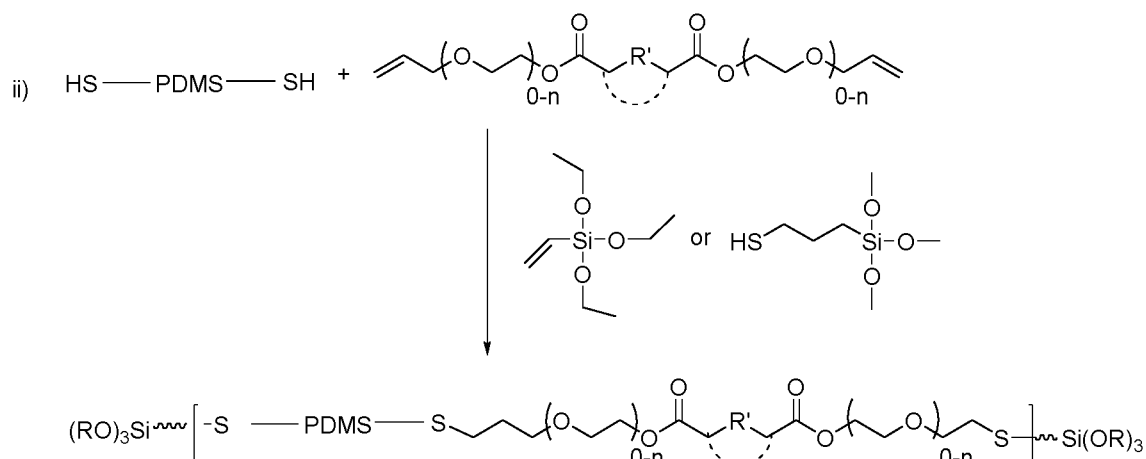


In a multi-neck flask with nitrogen line, stirring device and internal thermometer, succinic anhydride (50g, 0.5 mol), Diethylene glycol monoallyl ether (146.18 g, 1 mol) and Titanium (IV) butoxide (0.1 g) were dissolved in anhydrous xylene:



The mixture was stirred at 120 °C for 4h under nitrogen atmosphere. Xylene and all volatiles were removed by vacuum distillation (3h, 80 °C, 40 mbar).

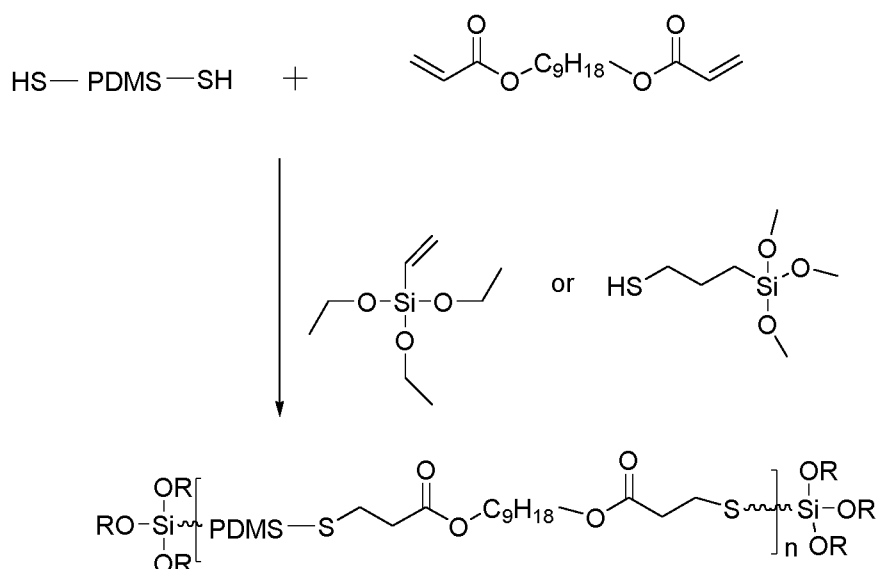
15 Example 5b General Scheme



In a multi-neck flask with nitrogen line, stirring device and internal thermometer, a,w-
 5 (mercaptopropyl) dimethylsiloxane copolymer (GP silicones, 100g, 0.026 mol-SH
 functionality), bis(2-(allyloxy)ethyl)succinate (10.03g, 0.036 mol), (3-
 Mercaptopropyl)trimethoxysilane (1.87g, 0.01 mol) and 2,2'-Azobis(2-
 methylpropionitrile) (100 mg) were dissolved in anhydrous xylene. The mixture was
 stirred at 70 °C for 5h under nitrogen atmosphere. Down-streamed Xylene and volatiles
 10 were removed by vacuum distillation (3h, 80 °C, 1 mbar).

GPC data: M_w 23853 g/mol, M_n 8085 g/mol, MWD 2.95 (Toluene, PS standards, 35°C)

Example 6: Siloxane-thiol + (meth)acryl terminated ester General scheme

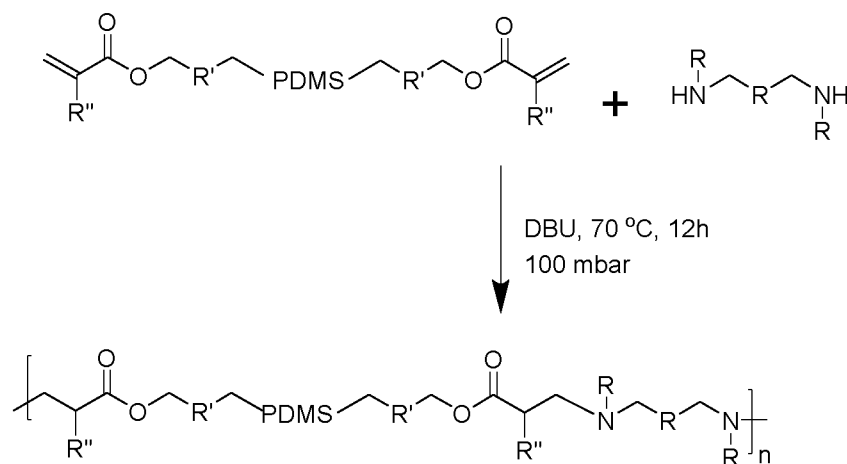


In a multi-neck flask with nitrogen line, stirring device and internal thermometer, a,w-(mercaptopropyl) dimethylsiloxane polymer (GP silicones 100g, 0.026 mol-SH functionality), Nonanediol Diacrylate (CAS-Nr.: 107481-28-7, TCI chemicals, 9.66 g, 0.036 mol), (3-Mercaptopropyl)trimethoxysilane (1.87, 0.01 mol) and 1,8-diaza-7-bicyclo[5.4.0]undecene (DBU) (0.109g, 0.1 wt%) were dissolved in anhydrous xylene. The mixture was stirred at 30 °C for 5h under nitrogen atmosphere. Xylene and other volatiles were removed by vacuum distillation (2h, 80 °C, 70 mbar).

GPC data: M_w 22643 g/mol, M_n 7522 g/mol, MWD 3.01 (Toluene, PS standards, 35°C)

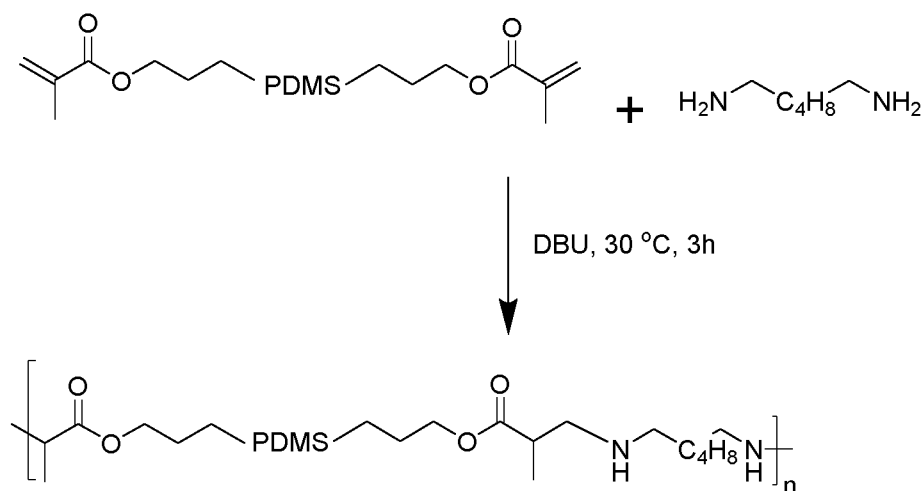
Example 7

10 (Meth)acrylate and amine functional monomers-Michael addition reactions – General Scheme



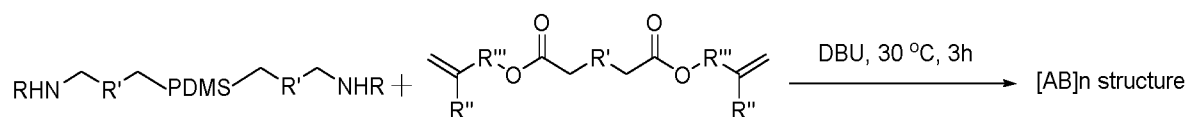
In a multi-neck flask with nitrogen line, stirring device and internal thermometer, methacryloxypropyl terminated polydimethylsiloxane (DMS-R18, CAS No. 58130-03-3, ABCR Chemicals) (150g, 0.0118 mol, vinyl), hexamethylenediamine (1.37g, 0.0118. mol) and 1,8-diaza-7-bicyclo[5.4.0]undecene (DBU) (0.15g, 0.1 wt%) were mixed. The mixture was stirred at 70 °C for 12h under 100 mbar vacuum.

GPC data: M_w 11449 g/mol, M_n 5030 g/mol, MWD 2.28 (Toluene, PS standards, 35°C)



Example 8 – General Scheme

5



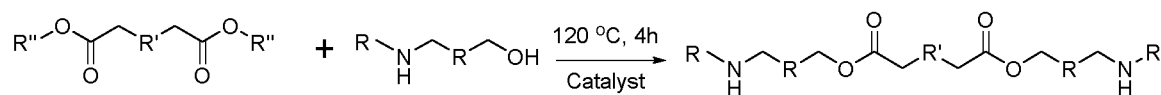
In a multi-neck flask with nitrogen line, stirring device and internal thermometer,
 10 Tegomer® A-Si 2322 (100g, 0.038 mol), dialylsuccinate (7.53g, 0.038 mol) and 1,8-diaza-7-bicyclo[5.4.0]undecene (DBU) (270 mg, 0.25 wt%) were dissolved in anhydrous xylene. The mixture was stirred at 30 °C for 3h under nitrogen atmosphere. Xylene was removed by vacuum distillation (3h, 80 °C, <1 mbar).

GPC data: M_w 7449 g/mol, M_n 3513 g/mol, MWD 2.12 (Toluene, PS standards, 35°C)

15

Example 9 PDMS-acrylate + amine- terminated ester general scheme

20



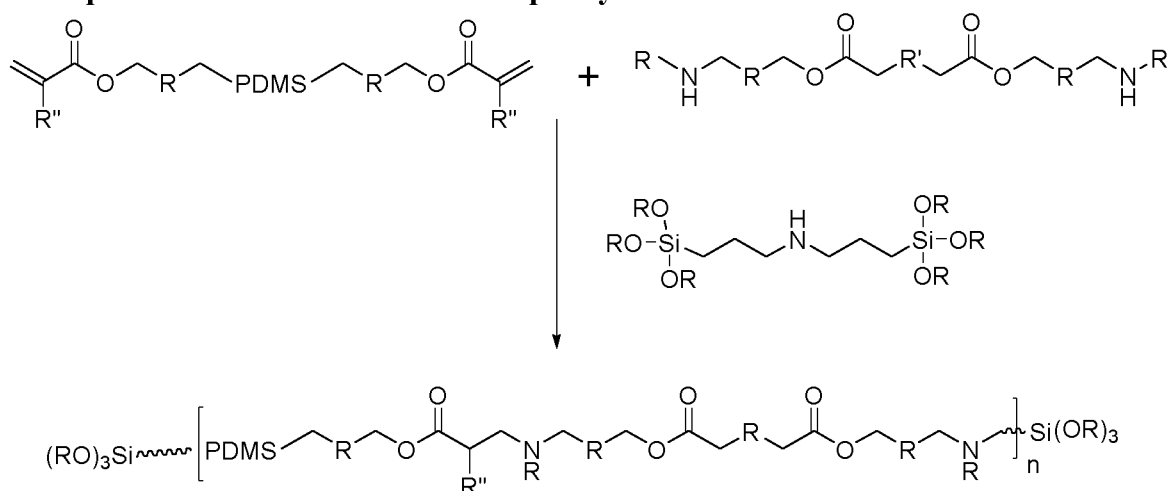
In a multi-neck flask with nitrogen line, stirring device and internal thermometer, dimethylsuccinate(50g, 0.34 mol), 2-(Methylamino)ethanol (10.94 g, 1.02 mol) and p-toluenesulphonic acid (0.1 g) were dissolved in xylene. The mixture was stirred at 120

°C for 4h under nitrogen stripping atmosphere to remove reaction water. Xylene and other volatiles (excess of alcohol) were removed by vacuum distillation (4h, 90 °C, <1 mbar).

GPC data: M_w 5449 g/mol, M_n 2162 g/mol, MWD 2.52 (Toluene, PS standards, 35°C)

5

Example 9b – General Scheme – One pot Synthesis

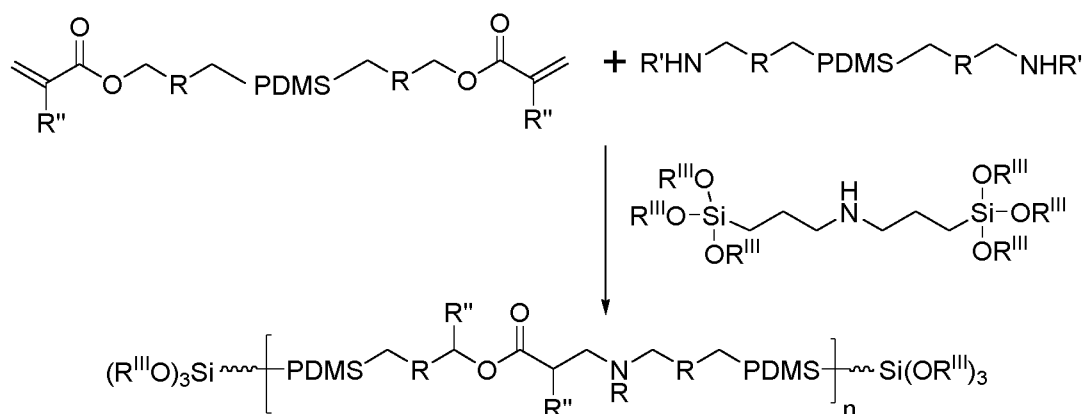


10 In a multi-neck flask with nitrogen line, stirring device and internal thermometer, methacryloxypropyl terminated polydimethylsiloxane (DMS-R18, CAS No. 58130-03-3, ABCR Chemicals) (100g, 0.022 mol), bis(2-(methylamino)ethyl) succinate (5.16g, 0.022 mol), Bis[3-(trimethoxysilyl)propyl]amine (Dynasylan® 1124) (1.72g, 5 mmol) and 1,8-diaza-7-bicyclo[5.4.0]undecene (DBU) (0.270 g, 0.25 wt.-%) were dissolved in
15 anhydrous xylene. The mixture was stirred at 30 °C for 3h under nitrogen atmosphere. Xylene and all other volatiles were removed by vacuum distillation (4h, 40 °C, <1 mbar).

GPC data: M_w 13954 g/mol, M_n 4828 g/mol, MWD 2.89 (Toluene, PS standards, 35°C)

20

Example 10: PDMS-Acrylate + PDMS-Amine



In a multi-neck flask with nitrogen line, stirring device and internal thermometer, methacryloxypropyl terminated polydimethylsiloxane (DMS-R18, CAS No. 58130-03-3, ABCR Chemicals) (100g, 0.022.mol), Tegomer® A-Si 2322 (57.7g, 0.022.mol), Bis[3-(trimethoxysilyl)propyl]amine (Dynasylan® 1124)(1.97, 0.006 mol) and 1,8-diaza-7-bicyclo[5.4.0]undecene (DBU) (0.394g, 0.25 wt%) were dissolved in anhydrous xylene. The mixture was stirred at 30 °C for 3h under nitrogen atmosphere. Xylene and volatiles were removed by vacuum distillation (4h, 40 °C, <0,1 mbar).

GPC data: M_w 12567 g/mol, M_n 4175 g/mol, MWD 3.01 (Toluene, PS standards, 35°C)

Example 11: Film forming experiment: PDMS based resin (example 3c) was cured at room temperature using 0.5 wt% TIB Kat 318. Neat resin was applied on a glass slide using a film applicator (Simex GmbH). Wet film thickness was 300 µm. Film was formed in 24h.

Claims

1. A fouling release coating composition comprising a binder and at least one additive oil, preferably in the absence of a biocide; or
an anti-fouling coating composition comprising a binder and at least one
5 marine anti-fouling agent,
wherein said binder comprises a polymer comprising a polysiloxane group, a plurality of ester groups, and a plurality of thio groups, amino groups or disulphide groups.
- 10 2. A coating composition as claimed in claim 1 wherein said binder comprises a polymer comprising in its backbone a plurality of polysiloxane groups, a plurality of ester groups, and a plurality of thio groups (e.g. of formula $-(C-S-CH_2)-$, such as $-(CH_2-S-CH_2)-$, amino groups (e.g. of formula $CH_2-NRa-CH_2-$) or S-S groups.
- 15 3. A coating composition as claimed in claim 1 wherein said binder comprises a polymer comprising in its backbone a repeating unit which comprises a plurality of polydimethylsiloxane groups, a plurality of ester groups, and a plurality of thio groups (such as those of formula $-(CH_2-S-CH_2)-$), amino or S-S groups
- 20 4. A coating composition as claimed in claim 1 wherein said binder comprises the reaction product of a vinyl terminated polysiloxane polyester monomer and a bithiol monomer or bisamino monomer, such as a thiol terminated polyester monomer or amino terminated polyester monomer.
- 25 5. A coating composition as claimed in claim 1 wherein said binder comprises the reaction product of a thiol terminated polysiloxane monomer and a vinyl terminated polyester monomer or thiol terminated polyester monomer.
- 30 6. A coating composition as claimed in claim 1 wherein said binder comprises the reaction product of a vinyl terminated polysiloxane monomer and a thiol terminated polyester monomer.

7. A coating composition as claimed in claim 1 wherein said binder comprises the reaction product of an amino terminated polysiloxane monomer and a vinyl terminated polyester monomer.

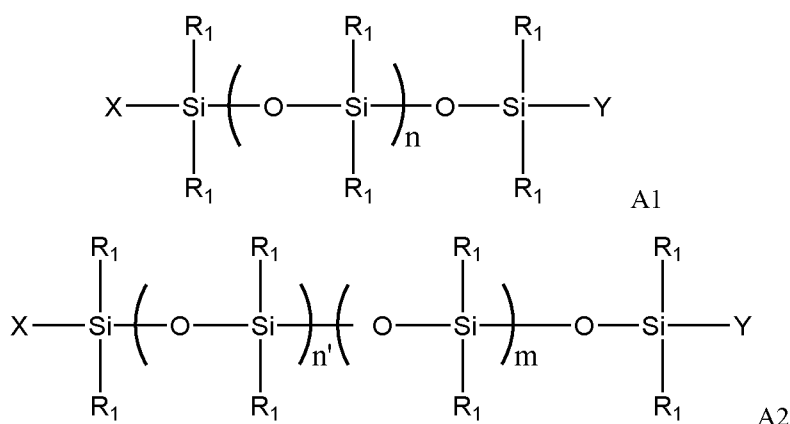
5 8. A coating composition as claimed in claim 4 to 7 wherein said vinyl group forms part of a (meth)acryloxyalkyl group.

9. A coating composition as claimed in claim 1 comprising the reaction product of a thiol terminated polysiloxane polyester monomer and a thiol terminated monomer, such a thiol terminated polyester monomer.

10

10. A binder for a coating composition comprising the reaction product of at least one polysiloxane monomer A' of general formula (A1)-(A2):

15



20

wherein each R₁ is the same or different and represents an unsubstituted or substituted C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₃₋₂₀ cycloalkyl, C₆₋₂₀ aryl, C₇₋₂₀ arylalkyl group, or a polyoxyalkylene chain;

25

X and Y can be the same or different and represent -CR=CH₂, -(CR''₂)_x·-CR=CH₂, -(CR''₂)_x·-CR''₂-OCO-CR=CH₂, -CR''₂-OCO-CR=CH₂, -(CR''₂)_x·-SH; -(CR''₂)_x·O-(CR''₂)_x·-SH, -(CR''₂)_x·[O-(CR''₂)_x]_f-OCO-CR=CH₂, -(CR''₂)_x·-(OR⁸)_a·-(OR⁸)_b-OR⁷-SH, -(CR''₂)_x·-(OR⁸)_a·-(OR⁸)_b-OR⁷-CR=CH₂, -CR''₂-Ar-CR''₂-SH, -(CR''₂)_x·C≡CH, -(CR''₂)_x·O-(CR''₂)_x·(CHOH)-(CR''₂)_x-OCO-CR=CH₂ or -(CR''₂)_x·-(OR⁸)_a·-(OR⁸)_b-OR⁷-C≡CH;

R'' is independently C₁₋₆ alkyl or H, especially H;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

each R is independently H or Me;

where R⁷ and R⁸ are each independently C₂₋₆ alkylene and a= 0-50, b= 0-50 and

5 a+b = 1-50;

f is 1 to 50;

Ar is C₆₋₁₂ aryl; and

n is 1-500, more preferably 10-300, especially 15-100;

or n' + m add to 1-500, more preferably 10-300, especially 15-100;

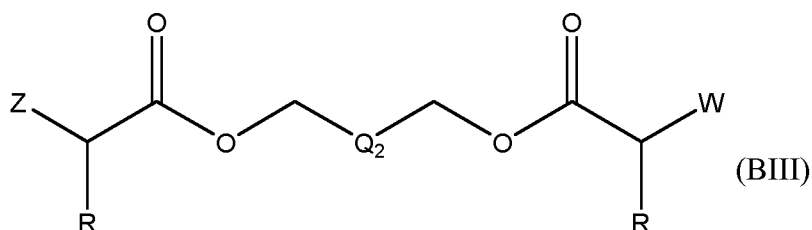
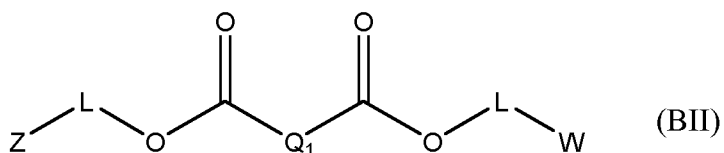
10 and at least one second monomer B' of formula

HS-Q3-SH (BI)

15 wherein Q3 is C₂₋₂₀ alkyl, C₃₋₂₀ cycloalkyl, phenyl, biphenyl, terphenyl, C₇₋₂₀ alkylaryl group, alkyl-polysiloxane-alkyl, C₄₋₂₀ alkylcycloalkyl or polyether;

wherein said C₂₋₂₀ alkyl, C₃₋₂₀ cycloalkyl, C₇₋₂₀ alkylaryl group, or C₄₋₂₀ alkylcycloalkyl optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

20 with the proviso that the SH groups in monomer B' react with the X and Y groups in ester containing monomer A' to form a group C-S-CH₂ or S-S group; or at least one second monomer B' of formula (BII) or (BIII)



wherein Q1 represents a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, a polyoxyalkylene chain of formula $R^7-(OR^8)_a-(OR^8)_b-OR^7$, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C4-10 alkylcycloalkyl;
 5 wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

L is C1-20 alkylene optionally comprising one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O or N, or a polyoxyalkylene chain
 10 of formula:



where R^7 and R^8 are each independently C₂₋₆ alkylene and $a=0-50$, $b=0-50$ and
 15 $a+b=1-50$;

R is H or Me;

Q2 is a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms
 20 selected from O, N, S or P, preferably O;

W and Z are -SH, $-(CR''_2)_xSH$, $CH_2=CR-$; $CH_2=CR-(CR''_2)_{x'}$ -, $-C\equiv CH$, -
 $NHCH_2-CR=CH_2$, $NHCH_2-CR\equiv CH-NHRa$, -NHRa or W and Z are $=CH_2$ (thus forming
 a double bond with the C atom to which W/Z is attached);

Ra is H or C1-6 alkyl wherein said alkyl group optionally comprises one or
 25 more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

R'' is independently C₁₋₆ alkyl or H, especially H;

x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

Ra is H or C1-6 alkyl wherein said alkyl group optionally comprises one or
 more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

30 with the proviso that the W and Z groups in monomer B' react with the X and Y groups monomer A' to form a group C-S-CH₂, an amino group or S-S group;

or at least one second monomer D' of formula:

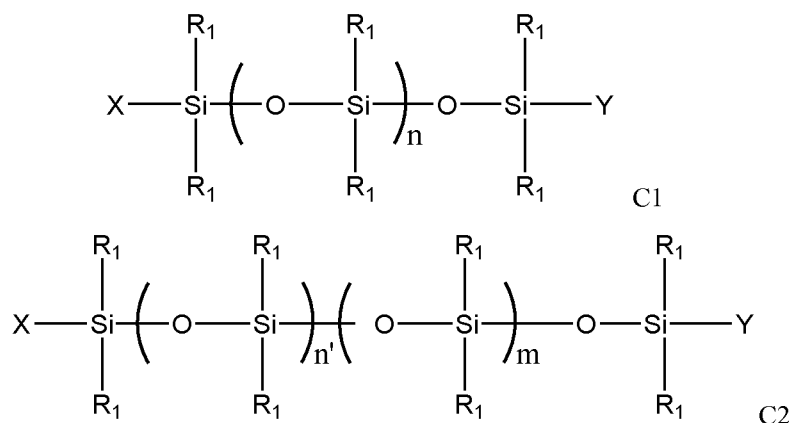
HRaN-Q5-NHRa (DI)

wherein Q5 is C2-20 alkyl, C2-20 alkenyl, C3-20 cycloalkyl, phenyl, biphenyl, terphenyl, Ph-O-Ph, C7-20 alkylaryl group, alkyl-polysiloxane-alkyl, C4-20 alkylcycloalkyl, C3-10 heterocyclic group or polyether (such as a $-(CH_2)_3O-(CH_2CH_2O)_r(CH(CH_3)CH_2O)_s(CH_2)_3-$ where $r+s$ is 1 to 100) wherein said C2-20 alkyl, C3-20 cycloalkyl, C7-20 alkylaryl group, or C4-20 alkylcycloalkyl optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

Ra is H or C1-6 alkyl;

with the proviso that the NRaH groups in monomer D' react with X and Y groups in ester containing monomer A' to form a group C-NRa-CH₂.

11. A binder for a coating composition comprising the reaction product of at least one polysiloxane monomer C' of general formula (C1)-(C2):



wherein each R₁ is the same or different and represents an unsubstituted or substituted C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₃₋₂₀ cycloalkyl, C₆₋₂₀ aryl, C₇₋₂₀ arylalkyl group, or a polyoxyalkylene chain;

X and Y can be the same or different and represent $-(CR''_2)_x-NRaH$, $-(CR''_2)_x-NH-(CR''_2)_x-NRaH$, $-(CR''_2)_x-(O-C2-6 \text{ alkyl})_x-NRaH$, $-(CR''_2)_x-O-(CR''_2)_x-NRaH$, or $-CR''_2-Ar-CR''_2-NRaH$;

R'' is independently C₁₋₆ alkyl or H, especially H;

R_a is H or C1-6 alkyl;

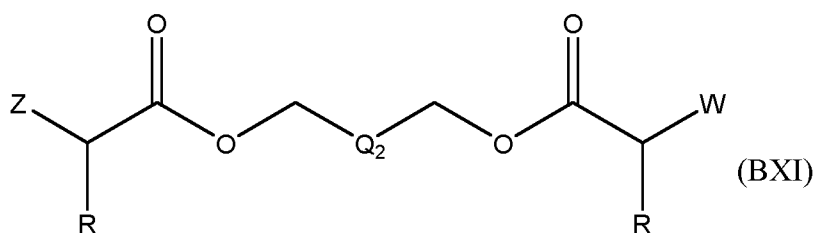
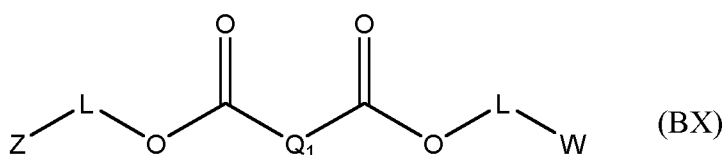
x' is 1 to 10, such as 1 to 5, especially 2 to 5, especially 3 to 5;

and

n is 1-500, more preferably 10-300, especially 15-100;

5 or n' + m add to 1-500, more preferably 10-300, especially 15-100; and

at least one second monomer B' of formula (BX) or (BXI)



10 wherein Q₁ represents a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, a polyoxyalkylene chain of formula R⁷-(OR⁸)_a-(OR⁸)_b-OR⁷, -Ph-O-C₁₋₆alkyl-OPh-, heterocycyl or C4-10 alkylcycloalkyl; wherein said C1-20 alkyl, C3-10 cycloalkyl, or C3-10 cycloalkenyl groups optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P,
 15 preferably O;

L is C1-20 alkylene optionally comprising one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O or N, or a polyoxyalkylene chain of formula:



where R⁷ and R⁸ are each independently C₂₋₆ alkylene and a = 0-50, b = 0-50 and a+b = 1-50;

R is H or Me;

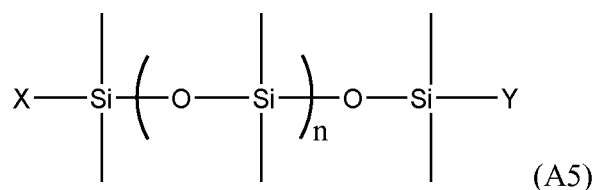
Q2 is a covalent bond, C1-20 alkyl, C3-10 cycloalkyl, C2-6 aminoglycol, C2-6 thioglycol, or C6-10 aryl wherein said C1-20 alkyl, C3-10 cycloalkyl, C3-10 cycloalkenyl, optionally comprise one or more, such as 1 to 4, heteroatoms selected from O, N, S or P, preferably O;

W and Z are $\text{CH}_2=\text{CR}-$; $\text{CH}_2=\text{CR}-\text{CH}_2-$, $\text{NHCH}_2-\text{CR}=\text{CH}_2$, $-\text{C}\equiv\text{CH}$, or W and Z are $=\text{CH}_2$ (thus forming a double bond with the C atom to which W/Z is attached);

with the proviso that the W and Z groups in monomer B' react with the amino X and Y groups in monomer C' to form a group $\text{C}-\text{NRa}-\text{CH}_2$.

10

12. A binder as claimed in claim 10 wherein monomer A' is of formula (A5):



15

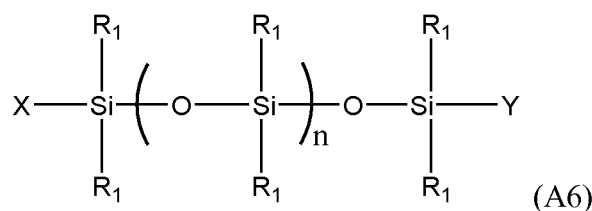
wherein,

X and Y are the same and represent $-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{O}-(\text{CH}_2)_{x'}-(\text{CHOH})-(\text{CH}_2)_x-\text{OCO}-\text{CR}=\text{CH}_2$ or $-(\text{CH}_2)_{x'}-\text{SH}$;

20

x' is 1 to 10, especially 2 to 5, such as 3 to 5; and

n is 10-300, especially 15-100; preferably of formula (A6):



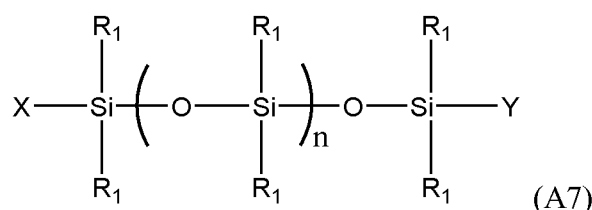
25

wherein each R_1 is methyl,

X and Y are the same and represent $-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)-(\text{CHOH})-(\text{CH}_2)-\text{OCO}-\text{CR}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$ or $-(\text{CH}_2)_{x'}-\text{SH}$;

x' is 1 to 5; and

5 n is 15-300; more preferably of formula (A7):



wherein each R_1 is methyl,

10 X and Y are the same and are $-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CH}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-\text{CH}_2-\text{OCO}-\text{CMe}=\text{CH}_2$, $-(\text{CH}_2)_{x'}-\text{SH}$.

x' is 1 to 5, especially 2 to 5, such as 3 to 5; and

n is 15-100.

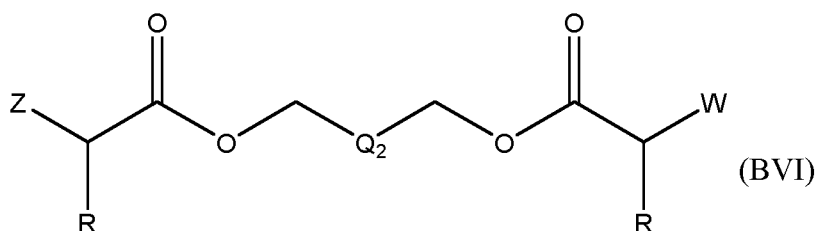
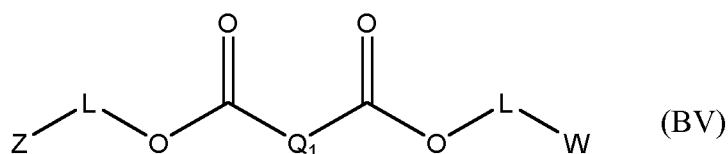
15

13. A binder as claimed in claim 10 or 12 wherein monomer B' is



20 wherein Q3 is represents a C2-16 alkylene, alkyl-polysiloxane-alkyl, or polyether group.

14. A binder as claimed in claim 10 wherein monomer B' is of formula BV or BVI

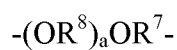


wherein Q1 is C2-10 alkyl, C3-8 cycloalkyl, C3-8 cycloalkenyl, C6-10 aryl, C7-
 5 12arylalkyl, or C4-10 alkylcycloalkyl.

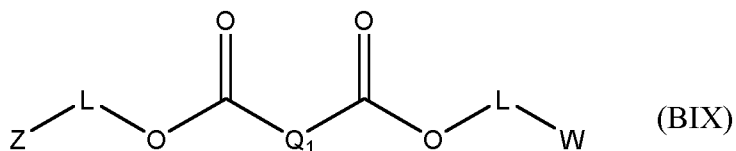
Q2 is a covalent bond, C1-10 alkyl, C3-8 cycloalkyl, C2-6 aminoglycol, C2-6
 thioglycol, or C6-10 aryl;

R is Me or H;

L is preferably C1-10 alkylene, such as C1-5 alkylene or a polyoxyalkylene
 10 chain of formula:



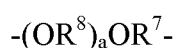
where R^7 and R^8 are each independently C_{2-6} alkylene and $a = 0-50$;
 15 W and Z are $-\text{SH}$, $-\text{CH}_2-\text{SH}$, $\text{CH}_2=\text{CR}-$; $\text{CH}_2=\text{CR}-\text{CH}_2-$, or W and Z are $=\text{CH}_2$,
 especially of formula of formula BIX



wherein Q1 is C2-10 alkyl, C3-8 cycloalkyl, C3-8 cycloalkenyl, C6-10 aryl, C7-12arylalkyl, or C4-10 alkylcycloalkyl;

R is Me or H;

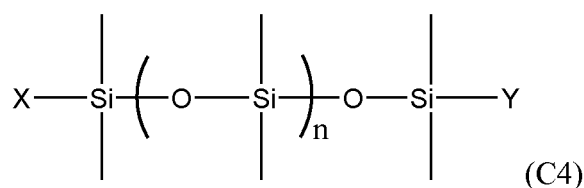
L is preferably C1-10 alkylene, such as C1-5 alkylene or a polyoxyalkylene
5 chain of formula:



where R^7 and R^8 are each independently C_{2-4} alkylene and $a = 0-50$;

10 W and Z are $-SH$, $-CH_2-SH$, $CH_2=CR-$; $CH_2=CR-CH_2-$, or W and Z are $=CH_2$.

15. A binder as claimed in claim 11 wherein monomer C'



15

X and Y groups are the same and are $-(CH_2)_{x'}-NH_2$, $-(CH_2)_{x'}-NH-(CH_2)_{x'}-NH_2$,
 $-(CH_2)_{x'}-O-(CH_2)_{x'}-NH_2$, $-(CH_2)_{x'}-O-(CH_2CH(CH_3))_{x'}-NH_2$;

x' is 1 to 5; and

n is 1-500, more preferably 10-300, especially 15-100.

20

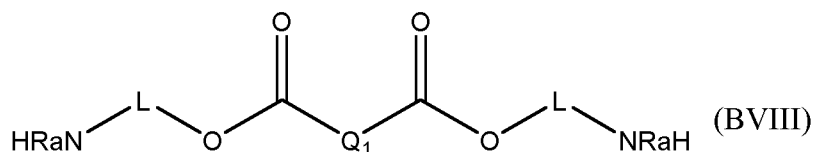
16. A binder as claimed in claim 10 wherein monomer D' is of formula



25

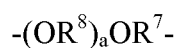
wherein Q5 is C2-10 alkyl, C1-6alkyl-polysiloxane-C1-6alkyl;

Ra is H or C1-6 alkyl; or wherein monomer B' is of formula BVIII



wherein Q₁ is C₂-10 alkyl, C₃-8 cycloalkyl, C₃-8 cycloalkenyl, C₆-10 aryl, C₇-12arylalkyl, or C₄-10 alkylcycloalkyl;

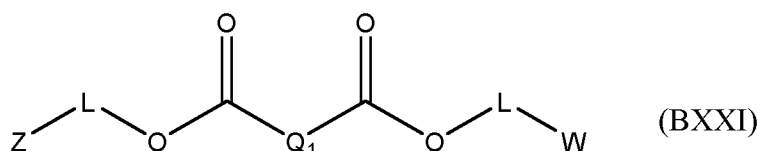
5 L is preferably C₁-10 alkylene, such as C₁-5 alkylene or a polyoxyalkylene chain of formula:



10 where R⁷ and R⁸ are each independently C₂₋₄ alkylene and a = 0-50; and Ra is H or C₁-6 alkyl.

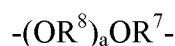
17. A binder as claimed in claim 11 wherein monomer B' is of formula (BXXI)

15



wherein Q₁ is C₂-10 alkyl, C₃-8 cycloalkyl, C₃-8 cycloalkenyl, C₆-10 aryl, C₇-12arylalkyl, or C₄-10 alkylcycloalkyl;

20 L is preferably C₁-10 alkylene, such as C₁-5 alkylene or a polyoxyalkylene chain of formula:



25 where R⁷ and R⁸ are each independently C₂₋₄ alkylene and a = 0-50; and R is H or Me;

W and Z are CH₂=CR-, CH₂=CR-CH₂-, -NHCH₂-CR=CH₂-, -C≡CH, or W and Z are =CH₂ (thus forming a double bond with the C atom to which W/Z is attached);

with the proviso that the W and Z groups in monomer B' react with the amino X and Y groups in monomer C' to form a C-NRa-CH₂- group.

18. A fouling release coating composition comprising a binder as claimed in claim 5 10 to 17 and at least one of filler, pigment, solvent, additive, curing agent and catalyst, preferably in the absence of a biocide;

or an anti-fouling coating composition comprising a binder as claimed in claim 10 to 17 and at least one anti-fouling agent.

10 19. An anti-fouling coating composition as claimed in claims 1 to 9 or 18 wherein the anti-fouling agent is selected from N2-tert-butyl-N4-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine (Cybutryne), 4,5- dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT, Sea-Nine® 211N), bis(l-hydroxy-2(lH)- pyridinethionato-0,S)-(T-4) zinc (zinc pyridinethione; zinc pyrithione), bis(l-hydroxy-2(lH)- pyridinethionato-0,S)-T-4) 15 copper (copper pyridinethione; copper pyrithione), zinc ethylene- 1,2-bis-dithiocarbamate (zinc-ethylene-N-N'-dithiocarbamate; Zineb), copper(I) oxide, metallic copper, copper thiocyanate, and cuprous sulfocyanate.

20. A process for protecting an object from fouling comprising coating at least a 20 part of said object which is subject to fouling with a coating composition as claimed in claim 1 to 9, 18 or 19 and preferably curing the composition.

21. An object coated with a coating composition as claimed in claim 1 to 9, 18 or 19, preferably a cured composition.