Claims

1. An antifouling coating composition comprising

(a) an ingredient having marine biocidal properties,

(b) a first copolymer comprising pendant to the polymer backbone, side chains A1, side chains B1 and optionally side chains C1, and

(c) a second copolymer comprising pendant to the polymer backbone, side chains A2, side chains C2, and optionally side chains B2,

wherein

side chains A1 and A2 may be same or different and comprise a non-metal salt group;

side chains B1 and B2 may be same or different and have the structure $–(Y)_n-R^3$;

side chains C1 and C2 may be same or different and have the structure $–(Y)_n-R^4$;

Y is –C(O)-O-, -C(O)-N(R^6)-, or -O-;

n is 0 or 1;

R^6 is H, a monovalent hydrocarbon group, or a bond to R^3 or R^4;

R^3 is a hydrocarbon group, optionally substituted with one or more heteroatoms selected from O, N, S, or a halogen group, wherein the total sum of carbon atoms in R^3 and R^6 in each of side chains B1 and B2 is 5 or more; and

R^4 is a hydrocarbon group, optionally substituted with one or more heteroatoms selected from O, N, S, or a halogen group wherein the total sum of carbon atoms in R^4 and R^6 in each of side chains C1 and C2 ranges from 1 to 4;

and wherein the molar ratio of $\frac{side\ chains\ B1}{\text{side chains B1+ side chains C1}}$ in the first copolymer > the molar ratio of $\frac{\text{side chains B2}}{\text{side chains B2+ side chains C2}}$ in the second copolymer.

2. The antifouling coating composition of claim 1 wherein

R^3 is a linear, branched or cyclic alkyl or aryl group, optionally substituted with one or more heteroatoms selected from O, N, S, or a halogen group, wherein the total sum of carbon atoms in R^3 and R^6 in each of side chains B1 and B2 is 5 or more; and

R^4 is a linear, branched or cyclic alkyl group, optionally substituted with one or more heteroatoms selected from O, N, S, or a halogen group wherein the total

sum of carbon atoms in R^4 and R^6 in each of side chains C1 and C2 ranges from 1 to 4.

3. The antifouling coating composition of any preceding claim wherein the non-metal salt group on side chains A1 and A2 comprise cations selected from quaternary ammonium groups or quaternary phosphonium groups, and anions selected from an anionic residue of an acid counter-ion having an aliphatic, aromatic, or alkaryl hydrocarbon group or a halide anion.

4. The antifouling coating composition of any preceding claim wherein the non-metal salt groups on side chains A1 and A2 are quaternary ammonium groups or quaternary phosphonium groups bound to the side chain of the polymer, the quaternary groups being neutralised by an anionic residue of an acid counter-ion having an aliphatic, aromatic, or alkaryl hydrocarbon group.

5. The antifouling coating composition of any preceding claim wherein the side chains A1 and A2 have the structure: $-(Y)_n-R^1-Z^{(+)}\ R^{2(-)}$

wherein
Y is –C(O)-O-, -C(O)-NH-, -O-;
n is 0 or 1;

R^1 is a divalent alkylene having 2 or 3 to 12 carbon atoms, Z is a quaternary ammonium group or quaternary phosphonium group and R^2 is an anionic residue of an acid counter having an aliphatic, aromatic, or alkaryl hydrocarbon group.

6. The antifouling coating composition according to claims 3 to 5 wherein the anionic residue of the acid counter-ion has an aliphatic, aromatic, or alkaryl hydrocarbon group comprising 6 or more carbon atoms.

7. Antifouling coating composition according to claims 3 to 6 wherein the counter-ions comprise 6 to 50 carbon atoms.

8. The antifouling coating composition of any preceding claim wherein the first copolymer and the second copolymer are poly(meth)acrylate or poly(meth)acrylamide copolymers.

9. The antifouling coating composition of any preceding claim wherein the molar ratio of $\frac{side\ chains\ B1}{\text{side chains B1+ side chains C1}}$ in the first copolymer is greater than or equal to 0.50, and the molar ratio of $\frac{side\ chains\ B2}{\text{side chains B2+ side chains C2}}$ in the second copolymer is less than 0.50.

10. The antifouling coating composition of any preceding claim wherein the molar ratio of $\frac{side\ chains\ B1}{\text{side chains B1+ side chains C1}}$ is greater than or equal to 0.60, and the molar ratio of $\frac{side\ chains\ B2}{\text{side chains B2+ side chains C2}}$ is less than 0.40.

11. The antifouling coating composition according to any preceding claim wherein
the mol% of side chains A1: mol% of side chains B1: mol% of side chains C1 in the first copolymer is 5-50: 50-95: 0-45, and
the mol% of side chains A2: mol% of side chains B2: mol% of side chains C2 in the second copolymer is 5-50: 0-45: 50-95,
wherein mol% in the first copolymer is based on the total sum of side chains A1+B1+C1 and mol% in the second copolymer in based on the total sum of side chains A2+B2+C2.

12. The antifouling coating composition of an preceding claim wherein R^3 is a linear, branched or cyclic alkyl or aryl group, optionally substituted with one or more heteroatoms selected from O, N, S, or a halogen group, wherein the total sum of carbon atoms in R^3 and R^6 in each of side chains B1 and B2 ranges between 5 and 40, preferably between 5 and 25.

13. An antifouling coating composition comprising
(a) an ingredient having marine biocidal properties,
(b) a first copolymer, and

(c) a second copolymer which is different to the first copolymer,

wherein the first copolymer is obtainable from at least monomers of Formula (I), monomers of Formula (II) and optionally monomers of Formula (III); and the second copolymer is obtainable from at least monomers of Formula (I), monomers of Formula (III) and optionally monomers of Formula (II), wherein

monomers of Formula (I) have the structure $CH_2=C(R^5)$-Y-$R^1Z^{(+)}$ $R^{2\,(-)}$;

monomers of Formula (II) have the structure $CH_2=C(R^5)$-Y-R^3;

monomers of Formula (III) have the structure $CH_2=C(R^5)$-Y-R^4; wherein

R^5 is H or CH_3,

Z is a quaternary ammonium group or quaternary phosphonium group;

Y is –C(O)-O-, -C(O)-NH-, -O-;

R^1 is a divalent alkylene having 2 or 3 to 12 carbon atoms;

R^2 is an anionic residue of an acid counter having an aliphatic, aromatic, or alkaryl hydrocarbon group;

R^3 is a hydrocarbon group, optionally substituted with one or more heteroatoms selected from O, N, S, or a halogen group, wherein the total sum of carbon atoms in R^3 and R^5 in the same monomer is 5 or more; and

R^4 is a hydrocarbon group, optionally substituted with one or more heteroatoms selected from O, N, S, or a halogen group, wherein the total sum of carbon atoms in R^4 and R^5 in the same monomer ranges from 1 to 4.

14. Method of providing a substrate with antifouling performance in an aqueous environment by

(a) providing the antifouling coating composition as defined in claims 1 to 13

(b) applying the coating composition to the substrate,

(c) allowing the coating composition to cure to form a coating layer,

(d) locating the substrate in coated substrate in the aqueous environment.

15. Use of the antifouling coating composition according to any one of claims 1 to 13 for protection of man-made structures immersed in water such as boat hulls, buoys, drilling platforms, oil production rigs, and pipes.