

AMPHIPHILIC BLOCK COPOLYMER FOR ANTIFOULING COATING

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application No. 61/202,303, filed February 17, 2009, the entire contents of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates generally to antifouling materials, and particularly to antifouling copolymers and coatings and methods of forming such copolymers and coatings.

BACKGROUND OF THE INVENTION

[0003] Self-assembling polymers and nano-structured polymer thin films are expected to be useful for marine and biomedical applications, such as for forming antifouling coatings.

[0004] Some specific copolymers have been proposed as potential antifouling materials. For example, Krishnan et al. reviewed a number of possible antifouling block copolymers. See. e.g., S. Krishnan et al., *J. Mater. Chem.*, 2008, vol. 18, pp. 3405-3413; S. Krishnan et al., *Langmuir*, 2006, vol. 22, pp. 5075-5086; S. Krishnan et al., *Biomacromolecules*, 2006, vol. 7, pp. 1449-1462.

SUMMARY OF THE INVENTION

[0005] There is a need for alternative antifouling materials and for antifouling materials with improved properties.

[0006] Accordingly, an aspect of the present invention provides an amphiphilic block copolymer for providing an antifouling surface. The block copolymer comprises a first polymeric block of repeat units and a second polymeric block of repeat units, copolymerized by living radical polymerization. The first block comprises hydrophilic antifouling side chains bonded to a first backbone segment. The first backbone segment has a length of 10 to 200 repeat units. The side chains have an average length of 5 to 23 monomer units. The repeat units in the first block have a polydispersity index of 1.3 or less, such as about 1.15. The second block comprises hydrophobic antifouling side groups bonded to a second backbone segment. The second backbone segment has a length of 10 to 200 repeat units, such as from 60 to 200 repeat units, or about 100 repeat units. The side groups of the second block may comprise fluorinated groups. The side chains of the first block may comprise poly(ethylene glycol). The copolymer may have a backbone segment formed of an acrylate group. The first block may comprise poly(ethylene glycol) methylether methacrylate and the second block may comprise poly(pentafluorostyrene). The first block may comprise poly(ethylene glycol) methylether acrylate and the second block may comprise poly(hexafluorobutyl methacrylate). The copolymer may comprise a third block of repeat units that is different from the first and second block.

[0007] In accordance with another aspect of the present invention, there is provided a method of forming the block copolymer described herein. In this method, a first precursor for the first block and a second precursor for the second block are copolymerized by living radical polymerization to form the block copolymer. The living radical polymerization may comprise atom transfer radical polymerization, or reversible addition-fragmentation chain transfer polymerization. The first precursor may be a polymer having a polydispersity index of 1.3 or less. The first precursor may be formed by living radical polymerization.

[0008] In accordance with another aspect of the present invention, there is provided a composition for providing an antifouling surface. The composition comprises an amphiphilic block copolymer comprising a first polymeric block of repeat units and a second polymeric block of repeat units. The first block comprises hydrophilic antifouling side chains bonded to a first backbone segment.

The first backbone segment has a length of 10 to 200 repeat units. The side chains have an average length of 5 to 23 monomer units. The repeat units in the first block have a polydispersity index of 1.3 or less, such as about 1.15. The second block comprises hydrophobic antifouling side groups bonded to a second backbone segment. The second backbone segment has a length of 10 to 200 repeat units, such as 60 to 200 repeat units, or about 100 repeat units. The block copolymer in the composition has a polydispersity index of 1.3 or less, and may be a block copolymer as described in the two preceding paragraphs.

[0009] In according to a further aspect of the present invention, there is provided an antifouling coating comprising the above composition. The antifouling coating may comprise a coating surface having inter-dispersed hydrophobic regions and hydrophilic regions. The hydrophobic regions are formed of the hydrophobic antifouling side groups of the block copolymer, and the hydrophilic regions are formed of the hydrophilic antifouling side chains of the block copolymer. One of the hydrophobic regions and the hydrophilic regions may form a continuous phase and the other of the hydrophobic regions and hydrophilic regions may form a dispersed phase. The dispersed regions may have an average size from 1 nanometer to 1 micrometer, such as about 20 nm.

[0010] In accordance with another aspect of the present invention, there is provided a solution comprising a solvent and the above composition dispersed in the solvent.

[0011] In accordance with a further aspect of the present invention, there is provided a method of forming an antifouling coating from the above solution. In this method, a layer of the solution is deposited on a surface; the solution is heated to facilitate phase separation in the solution; and the solvent is removed from the layer of the solution after the copolymer has phase separated to form separate hydrophilic and hydrophobic phases.

[0012] Other aspects and features of the present invention will become apparent to those of ordinary skill in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] In the figures, which illustrate, by way of example only, embodiments of the present invention,

[0014] **FIG. 1** is a perspective view of a coating on a substrate, exemplary of an embodiment of the present invention;

[0015] **FIG. 2** is a schematic diagram illustrating the structure of an amphiphilic block copolymer, exemplary of an embodiment of the present invention;

[0016] **FIG. 3** is a schematic diagram illustrating a synthesis route for preparing an exemplary amphiphilic block copolymer, exemplary of embodiments of the present invention;

[0017] **FIG. 4** is a schematic diagram illustrating a synthesis route for preparing another exemplary amphiphilic block copolymer, exemplary of embodiments of the present invention;

[0018] **FIG. 5** is a line graph showing representative ^1H -NMR spectra of the sample copolymer of **FIG. 3** in chloroform and water solvents respectively.

[0019] **FIG. 6** is a line graph showing the gas permeation chromatography (GPC) profiles of two sample materials;

[0020] **FIG. 7** is a line graph showing the relaxation time distribution function of a sample copolymer in a solution;

[0021] **FIG. 8** is a transmission electron microscopy (TEM) image of a sample material;

[0022] **FIG. 9** is a line graph showing the differential scanning calorimetry (DSC) curve of the sample copolymer of **FIG. 3**;

[0023] **FIG. 10** is an atomic force microscopy (AFM) height image of a sample film containing the sample copolymer of **FIG. 3**;

[0024] FIG. 11 is a TEM image of a sample film containing the sample copolymer of FIG. 3;

[0025] FIG. 12 is line graph showing ^1H NMR spectra of two sample materials;

[0026] FIG. 13 is a line graph showing GPC profiles of the sample materials of FIG. 12;

[0027] FIGS. 14 and 15 are AFM images of a sample film before and after water treatment, respectively;

[0028] FIG. 16 is a schematic diagram illustrating a procedure for preparation of sample coatings;

[0029] FIGS. 17, 18 and 19 are line graphs showing the time dependence of absorbed mass of different proteins on sample coatings; and

[0030] FIG. 20 is a schematic diagram of a micelle formed of an amphiphilic block copolymer.

DETAILED DESCRIPTION

[0031] FIG. 1 schematically illustrates an antifouling coating 100 formed on a substrate 102, exemplary of an embodiment of the present invention.

[0032] Substrate 102 may be formed of any material and may be part of a structure, such as underwater structure, that is to be protected against fouling. For example, the substrate material may include glass, silicon, metal, or the like.

[0033] Coating 100 has a coating surface 104, which has a hydrophilic phase and a hydrophobic phase. The two phases are formed by inter-dispersed regions 106 and 108. One of the two phases may be a continuous phase formed of interconnected regions, depicted in FIG. 1 as region 108, and the other phase may be formed of isolated regions, depicted in FIG. 1 as regions 106, which are dispersed in the continuous phase. In some embodiments, both phases may be formed of isolated regions. For convenience of description, it is assumed below that dispersed regions 106 are hydrophilic and form the hydrophilic phase, and the

continuous region **108** is hydrophobic and forms the hydrophobic phase. In some embodiments, the hydrophilicity of the continuous and dispersed phases may be reversed.

[0034] The inter-dispersed regions **106** and **108** have average sizes on the order of nano- to micrometer. The dispersed regions **106** have an average size from 1 nanometer to 1 micrometer. The average inter-distance between neighboring regions **106** is also from 1 nanometer to 1 micrometer. In a specific embodiment, the average region size may be about 20 nm.

[0035] Coating **100** may be formed of a composition that includes an amphiphilic block copolymer, such as copolymer **200** illustrated in **FIG. 2**, exemplary of an embodiment of the present invention.

[0036] Block copolymer **200** includes a hydrophilic (first) block of repeat units and a hydrophobic (second) block of repeat units. The hydrophilic block has a first backbone segment and hydrophilic antifouling side chains bonded to the first backbone segment. The hydrophobic block has a second backbone segment and hydrophobic antifouling side groups bonded to the second backbone segment. The hydrophilic antifouling side chains in the hydrophilic block form the hydrophilic regions **106** and the hydrophobic antifouling side groups in the hydrophobic block form the hydrophobic region **108**. The first backbone segment has a length of 10 to 200 repeat units. The second backbone segment has a length of 10 to 200 repeat units, such as 60 to 200 repeat units, or about 100 repeat units. The lengths of the two backbone segments may be independently selected. The side chains of the first block have an average length of 5 to 23 monomer units. In some embodiments, the side chains within the same copolymer molecule may have the same length.

[0037] The repeat units in the first block have a polydispersity index (PDI) of 1.3 or less, such as about 1.15. The block copolymer in the composition that is used to form the coating also has a PDI of 1.3 or less.

[0038] PDI is a measure of the distribution of molecular mass in a given polymer material. PDI may be calculated as the ratio of the weight average

molecular weight (M_w) to the number average molecular weight (M_n). The polydispersity of a given sample of polymer or copolymer may be conveniently determined by Gel-Permeation Chromatography (GPC) also known as Size Exclusion Chromatography (SEC). This technique measures both M_w and M_n of the sample, and determines the ratio of M_w/M_n from the measured values. A skilled person in the art will be able to readily perform these measurements for a given sample.

[0039] Antifouling materials, such as antifouling monomer groups, polymeric groups, or side chains, refer to monomer or polymer groups that can counteract or prevent the building up of deposits on underwater surfaces, such as the underwater surfaces of a ship or a marine structure. Substances that tend to form such deposits are referred to as foulants, which include cellular and proteinaceous materials. Some exemplary antifouling polymeric materials include silicone-poly(dimethylsiloxane) (PDMS), fluoropolymers, Zwitterionic-based polymers, poly(ethylene glycol) (PEG), polyvinyl acetate (PVA), polyacrylates, and oligosaccharides. The hydrophilic side chains may also be protein-repelling or resistant. For example, hydrophilic protein-repelling polymers such as Dextran (polysaccharide), poly(2-methyl-2-oxazoline) (PMOXA)), zwitterionic-polymers, or the like, may be used to form the side chains. The antifouling side chains and side groups in the block copolymer may be selected or formed from these and other known antifouling polymeric materials or monomer groups.

[0040] In some embodiments, the backbone segment in a block may be formed of acrylate monomer units, such as methacrylate units. In other embodiments, a vinylic backbone segment may also be used.

[0041] In some embodiments, the hydrophilic side chains in the first block may include PEG groups or other protein-repelling or resistant groups. For example, a repeat unit in the hydrophilic block may be a poly(ethylene glycol) acrylate (PEGMA), such as poly(ethylene glycol) methylether acrylate (PEGMEA), or poly(ethylene glycol) methylether methacrylate (PEGMEMA).

[0042] The repeat units in the first block may also include, for example, Zwitterionic polymers, such as sulfobetaine methacrylate methacrylate (SBMA) or

carboxybetaine methacrylate (CBMA); polysaccharides, such as Dextran; poly(oxazoline), such as PMOXA; poly(vinylpyrrolidone); or peptoids (*N*-substituted glycines).

[0043] In some embodiments, the side groups in the hydrophobic block may include fluorinated groups or fluoropolymeric groups. The hydrophobic block may be poly(pentafluorostyrene) (PPFS) or poly(hexafluorobutyl methacrylate) (PHFBMA). Fluoropolymers that can be used to form the second block include polymers formed from fluorine containing acrylates, methacrylates, or styrenes. For example, the fluoropolymer may be 2,2,3,3,3-pentafluoropropyl methacrylate, 2,2,3,3,4,4,4-Heptafluorobutyl methacrylate, 1H,1H,5H-octafluoropentyl acrylate, or difluorostyrene.

[0044] In some embodiments, the block copolymer may have only two blocks (diblock). In other embodiments, the block copolymer may have one or more other blocks, and can be, e.g. a tri-block copolymer. The additional block may be, e.g., an acrylate such as a methacrylate, or a PEG chain. In one embodiment, the copolymer is a tri-block copolymer with an additional PEG block that has 2 to 16 monomer units. The additional block(s) may be different from the first and second blocks.

[0045] In one embodiment, the hydrophilic block may be poly(PEGMA) or P(PEGMA) and the hydrophobic block may be PPFS, and the copolymer may be denoted as P(PEGMA)-*b*-PPFS. The copolymer may be formed by an ATRP process.

[0046] In a specific embodiment, the copolymer may be poly[poly(ethylene glycol) methylether methacrylate]-*block*-poly(pentafluorostyrene), or P(PEGMEMA)-*b*-PPFS. The PPFS may be poly(2,3,4,5,6-pentafluorostyrene). An example of such a block copolymer is the product shown in **FIG. 3**, where "X" is an halogen and can be, for example, Br or Cl; "m" and "n" are integers and may be independently selected from the range of 10 to 200.

[0047] In another embodiment, the hydrophilic block may be poly(PEGMEA), or P(PEGMEA), and the hydrophobic block may be PHFBMA.

[0048] In a specific embodiment, the copolymer may be poly[poly(ethylene glycol) methylether acrylate]-*block*-poly(2,2,3,4,4,4-hexafluorobutyl methacrylate), or P(PEGMEA)-*b*-PHFBMA. An example of such a block copolymer is the product shown in **FIG. 4**, where “m” and “n” are again integers and may be independently selected from the range of 10 to 200.

[0049] In different embodiments, the lengths of the PEG chains in the block copolymer may be different from the numbers shown in **FIGS. 2 and 3**. In an exemplary embodiment, the length of a terminal PEG chain may be from 2 to 16; and the average length of the PEG side chains attached to the backbone in a given copolymer may vary from 5 to 23.

[0050] The lengths of the backbone segments and the side chains in the block copolymer may be controlled to have relatively small variation over different copolymer molecules, so that surface **104** has well-defined nano- or micro-structures and patterns of regions **106** and **108**.

[0051] In this regard, the block copolymer, and its component polymeric blocks and side chains, may be formed by living radical polymerization (LRP).

[0052] Living radical polymerization techniques are generally known in the art, and involve the use of free radical chemistry in living polymerization. Common living radical polymerization techniques include atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, macromolecular design via the interchange of xanthates (MADIX) polymerization, nitroxide mediated radical polymerization (NMRP), and stable free radical mediated polymerization (SFRP). A skilled person in the art will readily understand how these techniques can be applied to form specific polymers or copolymers described herein, based on the guidance provided herein. The following references provide additional general guidance on these techniques: (1) C. J. Hawker et al., *Chemical Reviews*, 2001, vol. 101, p. 3661; (2) K. Matyjaszewski et al., *Chemical Reviews*, 2001, vol. 101, p. 2921; (3) J. Chiefari et al., *Macromolecules*, 1998, vol. 31, p. 5559; (4) D. Charmot et al., *Macromolecular Symposia*, 2000, vol. 150, pp. 23-32; (5) W. A. Braunecker et al., *Prog. Polym. Sci.*, 2007, vol. 32, pp. 93-146; (6) M. Ouchi et al., *Chemical Reviews*, 2009, vol. 109, pp. 4963-5050; (7) S. Yamago,

Chemical Reviews, 2009, vol. 109, pp. 5051-5068; (8) G. Moad et al., *Australian Journal of Chemistry*, 2009, vol. 62, pp. 1402-1472; (9) G. Moad et al., *Accounts of Chemical Research*, 2008, vol. 41, pp. 1133-1142; (10) T. Yamada et al., *Kobunshi Ronbunshu*, 2007, vol. 64, pp. 329-342; and (11) G. Moad et al., *Australian Journal of Chemistry*, 2005, vol. 58, pp. 379-410. Polymer materials produced by LRP conveniently have a low PDI, i.e., close to one (1).

[0053] The structures and sizes of regions **106** and their inter-region distances may be controlled by selecting appropriate lengths of the backbone segments and side chains in the block copolymer. For example, increasing the lengths of the hydrophilic backbone segment and the side chains can increase the sizes of regions **106**; and increasing the length of the hydrophobic backbone segment can increase the inter-region distances between regions **106**. Changes in the polymer lengths can also affect the heights of the protruded portions in the coating.

[0054] The length of each block in the block copolymer can be controlled during the formation process by adjusting the ratio of monomer to initiator for each block, or by varying polymerization reaction time for each polymeric component (block) (thus controlling the percentage of converted monomers. For example, the polymerization reaction may be terminated at a selected time by exposing the reaction mixture to air or changing the environmental conditions (such as temperature). The side chain length can be controlled by using different monomers with different side chain length.

[0055] When the backbone lengths and the side chain lengths in the block copolymer are limited to within relatively narrow ranges and the block copolymer is produced by living radical polymerization with a PDI close to 1, the copolymer can have well-defined, brush-like polymeric structures. As used herein, a brush-like structure refers to a copolymer structure that has a first block with long side chains attached to a first backbone segment and a second block with a second backbone segment but without long side chains, wherein the long side chains have chain lengths within a relatively narrow range and are distributed along the first backbone segment, thus resembling the bristles on a typical brush. In a brush-like polymer,

the long side chains are typically are densely distributed along the backbone. For example, each backbone unit in the first block may have one long side chain. A long side chain is a side chain with more than four monomer units. The long side chains in a well-defined brush-like block copolymer may have the same length.

[0056] Thus, the block copolymer in the composition used to form coating **100** should have a PDI of 1.3 or less. This may be achieved by requiring that the repeat units in the hydrophilic block to have a PDI of 1.3 or less, such as about 1.15; the hydrophilic side chains in the copolymer to have a PDI of 1.3 or less; and the repeat units of the hydrophobic block to also have a PDI of 1.3 or less.

[0057] Coating **100** may be conveniently formed according to the following process, exemplary of an embodiment of the present invention. The block copolymer is dispersed or dissolved in a solution. A layer of the solution is deposited on the surface that is to be coated, such as the top surface of substrate **100**. For this purpose, the solvent in the solution may be an organic solvent or water. Suitable organic solvents may include tetrahydrofuran (THF), 1,4-dioxane, chloroform, trifluorotoluene, or the like. The solution may be deposited using any suitable technique, such as spin coating, dip-coating, drop-deposition, or the like.

[0058] Conveniently, the block copolymers can self-assemble and undergo phase separation on the surface under suitable conditions. The solution may be heated to a suitable temperature, such as above 100 °C, to facilitate phase separation in the solution. After the copolymer has phase separated to form separate hydrophilic and hydrophobic phases, the remaining solvent may be removed, such as by evaporation.

[0059] For instance, the solvent may be evaporated and the deposited layer may be subject to heat treatment by solvent annealing or annealing above the glass transition temperatures (T_g) of both the first and second blocks. For example, the layer may be heated to a temperature above about 100 °C when the block copolymer contains PPFS as the second block. Such treatments can lead to thermodynamically stable phase separation of the hydrophilic and hydrophobic phases. In this regard, the solvent may be selected with a view that it would provide favorable thermodynamics for both hydrophilic and hydrophobic blocks in

the copolymer. For example, both PEG and fluoropolymer may be dissolved in an organic solvent such as THF, 1,4-dioxane, chloroform, trifluorotoluene, or the like.

[0060] In a solution in which the solvent (such as water) favors one block (such as the hydrophilic block) over the other block (such as the hydrophobic block), the block copolymer may also self-assemble into nano-particles in the solution, known as micelles.

[0061] Conveniently, after removal of the solvent, the resulting coating has well-defined nano-patterns of inter-dispersed hydrophilic and hydrophobic antifouling regions.

[0062] The block copolymer may be attached to substrate surface through chemical bonding between a surface material and a suitable group in the copolymer. The substrate surface may be treated before coating to provide anchoring surface molecules for this purpose. For example, the substrate surface may be treated to provide amino (NH₂) groups attached to the surface. Conveniently, when the copolymer includes a PPFS block, the copolymer may bond with the surface through nucleophilic substitution reaction between *para*-F atoms in pentafluorostyrene and the amino groups that have been attached to the surface.

[0063] When an organic solvent is used, the coating may have discrete and dispersed hydrophilic regions and a continuous hydrophobic region, as in coating **100** shown in **FIG. 1**.

[0064] It is also possible to form a coating with discrete and dispersed hydrophobic regions and a continuous hydrophilic region. To form such a coating, the above process may be modified by using a polar solvent. For example, an aqueous solution may be used to form the initial layer on the surface. In this case, the hydrophobic blocks will form the dispersed phase and the hydrophilic blocks will form the continuous phase.

[0065] Regardless, the different regions (domains) on the coating surface may have characteristic sizes on the order of nanometer to micrometer. In one embodiment, the domain sizes may be about 20 nm. Domain sizes refer to the

average diameters of the substantially circular discrete domains, which are, for example, formed of distinct and visible features in a microscopic image. The size of a domain of the continuous phase may be considered as the average distance between closest adjacent domains of the discrete phase. The domain sizes can be measured using any suitable technique. For example, section analysis in Atomic Force Microscopy (AFM), Optical Microscopy, and Transmission Electron Microscopy (TEM) may be used to determine the domain sizes. In one embodiment, the domain sizes may be measured using AFM section analysis.

[0066] The resulting coating may have a well-defined nanostructure.

[0067] A further embodiment relates to a method of forming the block copolymer described herein. In this method, precursor polymers for respective hydrophilic and hydrophobic blocks are separately obtained or prepared, and then copolymerized to form the copolymer by living radical polymerization, such as ATRP or RAFT. To better control the polydispersity in the resulting copolymer, precursor polymers with low PDI may be selected. For example, a precursor polymer may have a PDI of 1.3 or less, such as about 1.15. The precursor polymers may be formed by living radical polymerization to better control their polydispersity and other properties.

[0068] In an exemplary embodiment, the component polymeric blocks and side chains in the block copolymer may all be formed by living radical polymerization to better control the polydispersity of the resulting products and the uniformity of the side chain lengths and backbone lengths. Conveniently, an antifouling coating formed with such copolymers can have well-defined inter-dispersed hydrophilic and hydrophobic regions on the coating surface.

[0069] Exemplary embodiments of the present invention also relate to compositions that include a block copolymer described herein.

[0070] Exemplary embodiments of the present invention also relate to methods for forming the copolymers disclosed herein. In an exemplary process, a first precursor for the hydrophilic block and a second precursor for the hydrophobic block are obtained and copolymerized by living radical polymerization to form the

block copolymer. The living radical polymerization may be atom transfer radical polymerization, reversible addition-fragmentation chain transfer polymerization. The first precursor for the hydrophilic block may be selected to have PDI of 1.3 or less, so that the resulting copolymer will have a PDI of 1.3 or less. To this end, the first precursor may be formed by living radical polymerization.

[0071] The exemplary synthesis processes are further illustrated in the Examples. As can be appreciated, the specific procedures and synthesis routes for a given copolymer may differ from those described in the Examples depending on the particular polymeric components used. However, a person skilled in the art will be able to modify the example processes for forming any given copolymer based on the guidance provided therein.

[0072] The coating conveniently has antifouling properties and can, for example, discourage barnacle settlement.

[0073] Conveniently, the coating surface is heterogeneous and is expected to be useful for reducing settlement of various biomaterials and for enhancing release of fouling organisms. As the amphiphilic block copolymer can self-assemble, it provides a versatile bottom up approach to form non-biofouling heterogeneous surfaces. The block copolymers described herein, and compositions and coatings formed from such copolymers may thus have application in various fields including marine- or bio-antifouling.

[0074] For example, fluoropolymer and PEG components are expected to be effective in reducing settlement and increasing release of marine algae, such as *Ulva*, or *Navicula*. Without being limited to any particular theory, it is expected that the coating surfaces formed of such copolymers are energetically unfavorable for protein and glycoprotein adsorption, thus weakening the adhesive strength of an entire foreign organism to the coated surface. For example, PPFS segments can provide characteristics such as low surface energy, high chemical and thermal resistance, and distinctive self-assembly behavior. P(PEGMA) segments can potentially introduce other desirable properties to the copolymers such as water solubility, low toxicity, high biocompatibility and fouling resistance to proteins.

[0075] Exemplary copolymers, compositions, and coatings described herein may be used in marine anti-fouling applications, such as for forming non-toxic, environment-friendly anti-fouling coatings. The coatings may be applied to underwater structures such as ship hulls. The coatings may conveniently have improved lifetime, mechanical properties, or chemical/mechanical stability, as compared to some coatings formed of other antifouling polymers such as polydimethylsiloxane elastomers, PEG, existing fluoropolymers, and particulate organic matter (POMS). As compared to coatings formed of a PEG polymer or a fluoropolymer, a coating formed of an amphiphilic block copolymer described herein is more versatile, as the latter can be effective against a wider variety of foulants, such as various plants, algae, animals, bacteria, microorganisms, or the like.

[0076] It is expected that exemplary embodiments of the block copolymers described herein can be used to form an efficient, non-toxic, antifouling coating, without relying on biocide release. As the block copolymers used to form the coating can have a well-defined structure and a low molecular weight distribution, it is easier to control the bulk properties of the materials used to form the coating, which may include mechanical strength, morphology, surface energy, or the like. The structures of the block copolymers are such that non-specific adsorption of various biomacromolecular adhesives can be reduced or minimized on a micro- or nano-scale. The block copolymer may be effective against many biomacromolecular adhesives released by various marine organisms, such as protein, glycoprotein, lipopolysaccharide, or the like. The coating formed from the block copolymers may also facilitate the release of any marine organism attached to the coating, as, for example, the fluoropolymer segments have low surface energy and consequently it requires less energy to remove any attached fouling organisms from the coated surface.

[0077] When the amphiphilic block copolymers provide nano-scale patterned antifouling structures, which may be brush-like, it is expected that antifouling efficiency against certain foulants can be increased as compared to antifouling materials that have larger structures such as micro-scale structures which are linear or branched. For example, it is expected that many marine foulants

are less likely to settle and grow on a surface formed by the amphiphilic block copolymers with nano-scale antifouling features.

[0078] When the block copolymer is formed with a living radical polymerization process, such as ATRP or RAFT, it is convenient to control the structures and certain properties of the resulting product. For example, the resulting product may have a well-defined brush-like structure and a low polydispersity index. As the chemical structure of the product can be conveniently controlled, the product's bulk material properties such as mechanical strength, surface energy, and morphology can also be conveniently controlled.

[0079] In exemplary embodiments of the block copolymer, the protein-resistant or repelling segments can be arranged in the most efficient manner. A brush-like structure can provide optimal surface area exposure, thus resulting enhanced antifouling behavior.

[0080] The surface energies between different individual blocks in the copolymer can be quite large. When the copolymer is used to form antifouling coatings, a large surface energy difference between different blocks can lead to self-assembled micro/nano phase separated surface structures with well-defined hydrophobic and hydrophilic domains. These nano-patterns can create high potential energy topography unfavorable for biomacromolecule settlement by disruption of the protein-surface interactions occurring on nanoscale dimension. It is expected that such patterned surfaces can minimize non-specific adsorption of biomacromolecules, including proteins, glycoproteins and lipopolysaccharides. These biomacromolecular adhesives (protein/glycoprotein/lipopolysaccharide) may have affinities for either hydrophobic or hydrophilic surfaces.

[0081] The use of fluorinated blocks allows optimization of the surface free energy, such as to the range of 35 to 40 mJ/m² (corresponding to water contact angles of about 60 to about 80°), and reduction of work of adhesion between the surface and the marine organism ($W_{\text{adhesion}} \propto \text{surface energy}$), thereby facilitating the release of attached marine organisms under a minimal force such the shear force generated by the movement of a ship in water at the speed of about 30 to 40 knots. Thus, these copolymers can potentially be used as (a) environmentally

friendly, non-toxic marine anti-fouling coatings, (b) anti-biofouling surfaces for the modification of biological implants, (c) patterned thin films for biosensing as well as encapsulation and release applications. Nanoscopic micelles comprising these block co-polymers could be used as (a) precursors to shell-crosslinked/core-crosslinked nanoparticles for drug delivery; (b) emulsion stabilizers; (c) rheology modifiers in the cosmetic industry or (d) nano-reactors in selective solvents.

[0082] Exemplary embodiments of the present invention are further illustrated with the following examples, which are not intended to be limiting.

[0083] EXAMPLES

[0084] Starting materials mentioned in these examples were obtained as follows, unless otherwise specified. Methoxy poly(ethylene glycol) with $M_n = 750$ g/mol (referred to as MPEG750 herein), MPEG methacrylate ($M_n = 1100$ g/mol), 2-bromoisobutyryl bromide (98%), anhydrous trifluorotoluene (99%), *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) (99%), and 2,3,4,5,6-pentafluorostyrene (99%) were obtained from Aldrich™. 2,3,4,5,6-Pentafluorostyrene was used after passing through alumina column to remove stabilizer therein. Triethylamine (99.7%) was obtained from Fisher™, and dried over molecular sieves before use. 2,2-bipyridine (99+ %) was obtained from Strem Chemicals™. CuCl, and CuCl₂ (99%) was obtained from Alfa Aesar™.

[0085] The starting materials were used as received, unless otherwise specified.

[0086] Proteins (BSA, $M_w = 66\,000$ Da; LPSE, $M_w = 10\,000$ Da; and CFL, $M_w = 60\,000$ Da) were purchased from Aldrich.

[0087] ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer.

[0088] GPC analyses were carried out in THF at 35 °C with a flow rate of 1 mL/min using a Waters 2690 system fitted with an evaporative light scattering detector (Waters 2420). A series of three phenomenox linear 5 μm Styragel columns (500, 10⁴, and 10⁶ Å) were used for the separations. The GPC was calibrated against polystyrene standards.

[0089] Transmission electron microscopy (TEM) images were obtained using a JEOL 2100 transmission electron microscope operating at an acceleration voltage of 200 kV. The TEM samples were prepared by dip-coating a carbon coated copper grid with the respective solution.

[0090] Fluorescence measurements were carried out on a LS50B luminescence spectrometer (Perkin-Elmer).

[0091] A Brookhaven BI-9000AT Digital Autocorrelator was used for the differential light scattering (DLS) measurements (using a vertically polarized laser light of wavelength 632.8 nm). The DLS measurements were made with the intensity correlation function measured at a temperature of 25 °C (unless otherwise stated) with a maximum number of 256-channels using a BI-9000AT digital autocorrelator.

[0092] Example I. Synthesis of Sample I, P(PEGMEMA)-*b*-PPFS

[0093] Sample I was prepared according to the synthesis route illustrated in **FIG. 3**, and as further described next.

[0094] An ATRP initiator was prepared as follows. MPEG750 (0.133 mmol) was dissolved in dried THF (~30 mL) in a two neck round bottom flask under argon equipped with magnetic stirrer bar, followed by the addition of triethylamine (0.285 mmol) by syringe. The solution was then cooled in ice/salt mixture and stoichiometric amount of 2-bromoisobutyryl bromide was added drop wise. The reaction continued overnight under argon atmosphere at room temperature. After filtration and evaporating solvent, the product was dissolved in water and extracted with dichloromethane in several steps. A yellowish oily product was recovered after drying over MgSO₄ and drying under vacuum at 40 °C. This product is referred to herein as "MPEG750 initiator".

[0095] Samples of poly(polyethylene glycol methylether methacrylate) (P(PEGMEMA)) were typically prepared by ATRP as follows. MPEG750 initiator (0.11 mmol) and MPEG methacrylate ($M_n=1100$, 4.73 mmol) were dissolved in a water/methanol mixture (4 mL water + 1 mL methanol) in a schlenk tube equipped with a magnetic stirrer bar. The solution was deoxygenated by freeze-pump-thaw

cycles, followed by addition of CuCl, CuCl₂, and 2,2-bipyridine (molar ratio was maintained as: initiator : Cu(0.6CuCl + 0.4CuCl₂) : 2,2-bipyridine = 1 : 1 : 3), under argon. The polymerization was performed at room temperature under argon and terminated at designated times by exposure to air and dilution with THF. The polymerization solution was then purified on an alumina column to remove copper catalyst. Excess solvent was removed by rotary evaporation and the solid product was recovered after precipitation in hexane and drying in vacuum at 40 °C overnight. The product was recovered after precipitation in hexane and drying under vacuum at overnight. This product is referred to as "P(PEGMEMA) sample".

[0096] In the subsequent chain extension procedure, sample P(PEGMEMA)-*b*-PPFS diblock copolymer was formed by ATRP using the P(PEGMEMA) sample as macroinitiator. P(PEGMEMA) sample (0.053 mmol) and pentafluorostyrene (15.2 mmol) were mixed in a schlenk tube and deoxygenated by four freeze-pump-thaw cycles. CuBr and PMDETA (1:1 molar ratio) were then added to the mixture under argon. The contents were further deoxygenated by one more freeze-pump-thaw cycle. The schlenk tube was transferred to an oil bath maintained at 100 °C. Chain extensions occurred at 100 °C, as evidenced by the attainment of high solution viscosities. Polymerizations was terminated by THF dilution and exposure to air, prior to copper removal on alumina columns. The block copolymer products (white powder) were recovered after precipitation in hexane and drying overnight in vacuo at 50 °C. The resulting Sample I copolymer was a brush-like amphiphilic diblock copolymer of P(PEGMEMA)-*b*-PPFS (see **FIGS. 2 and 3**).

[0097] Example II. Synthesis of Sample II, P(PEGMEA)-*b*-PHFBMA

[0098] Sample II was prepared according to the synthesis route illustrated in **FIG. 4**, and as further described next.

[0099] PHFBMA homopolymer samples were formed by RAFT. In a schlenk reaction tube, a mixture of HFBMA, cyanopropyl dithiobenzoate (CPDB), and azobisisobutyronitrile (AIBN) was formed with molar ratios of [HFBMA]/[CPDB] = 250 and [CPDB]/[AIBN] = 3. The reaction mixture was degassed by 5 freeze-pump-thaw cycles and placed in an oil bath pre-heated at 70 °C. After about 150

minutes of heating, the reaction mixture was quenched by placing the tube in liquid nitrogen. The crude polymer was precipitated in cold hexane to remove oligomers and unreacted monomer. Pure PHFBMA polymer sample was obtained by filtering the precipitate and drying under vacuum for 15 hrs at room temperature.

[00100] P(PEGMEA)-*b*-PHFBMA copolymer samples were formed by RAFT. A mixture of PHFBMA, PEGMEA, and AIBN was dissolved in trifluorotoluene and transferred to a schlenk reaction tube which was sealed and degassed by 5 freeze-pump-thaw cycles to remove traces of oxygen. The typical molar ratios in the mixture were [PEGMEA]/[PHFBMA] = 200 and [PHFBMA]/[AIBN] = 3. The reaction tube was then placed in an oil bath pre-heated at 70 °C for 4 hours. The reaction was quenched by placing the tube in liquid nitrogen and precipitated in diethyl ether. The cloudy ether solution was centrifuged to remove the pure polymer by decanting the supernatant solution. The polymer deposit was collected by re-dissolving the crude product in chloroform and isolated by evaporation of the solvent followed by drying under vacuum for 24 hours.

[00101] Different batches of Sample II with controlled molecular weights were obtained by using different molar ratios of monomer to the chain transfer agent.

[00102] Example III. Characterization of Sample I, P(PEGMEMA)-*b*-PPFS)

[00103] Sample I copolymer was dissolved in an aqueous solution and an organic solution respectively. The solvents were deuterated (denoted by "*d*"). Self-assembled micelles with PPFS segments in the central regions (core) and P(PEGMEMA) segments in the peripheral regions (corona) were observed in the aqueous solution.

[00104] Representative ¹H NMR spectra of Sample I co-polymer in both *d*-chloroform (top) and *d*-water (bottom) are shown in **FIG. 5**, which also show the peak assignments. In *d*-chloroform, the chemical shifts *a* ($\delta \sim 0.7 - 1.1$ ppm), *b* ($\delta \sim 3.4$ ppm), and *c* ($\delta \sim 3.6 - 4.2$ ppm) can be assigned, respectively, to protons from the methyl group (-CH₃) attached to P(PEGMEMA) backbone, methoxy (-OCH₃) and methylene (-O-CH₂-CH₂-) protons of the PEG side chains of P(PEGMEMA) block and the PEG initiator combined. Signals *d* ($\delta \sim 1.7 - 2.8$ ppm) represent

backbone protons of the PPFS block in copolymer. ^1H -NMR signals of PEG were observed in *d*-water, but signals due to PPFS block were absent, which suggested the formation of micellar aggregates by P(PEGMEMMA)-*b*-PPFS block copolymer in water with PPFS buried in the micelle core (not accessible to NMR) and PEGMEMA chains constitute the corona. This also indicates that the sample was indeed an amphiphilic diblock copolymer.

[00105] Gas permeation chromatography (GPC) profiles of Sample I (solid line) and the P(PEGMEMMA) macroinitiator (dotted line) were obtained against polystyrene standards in THF as eluant. Representative GPC profiles are shown in **FIG. 6**.

[00106] It was determined the P(PEGMEMMA) macroinitiator prepared in Example I had an M_n of about 11400 g/mol, and a PDI of about 1.15; Sample I copolymer had an M_n of about 31000 g/mol, and a PDI of about 1.3.

[00107] Relaxation time (τ) distribution functions were obtained from dynamic light scattering (DLS) measurements of the sample solutions at scattering angle 90° . A representative distribution function is shown in **FIG. 7**, which was obtained from a solution with a copolymer concentration of 0.5 mg/ml. As can be seen, the function is unimodal (with one peak), suggesting the formation of micellar aggregates with narrow particle size distribution in the solutions. The hydrodynamic particle size of P(PEGMEMMA)-*b*-PPFS block copolymer micelle in an aqueous solution was measured using DLS, and it was found to be about 56 nm.

[00108] Angle dependent measurements produced insignificant difference in the hydrodynamic size of the micelles, confirming that the aggregates or particles were of generally spherical shape (characteristics of micellar aggregates).

[00109] The spherical shapes were confirmed by the TEM image shown in **FIG. 8**, which was obtained from micelles transferred from the aqueous solution to a carbon film. In the TEM image, the darker regions represent polymer segments with higher electron density. Thus, in **FIG. 8**, the darker core represents the PPFS segments and the lighter bands around the dark cores represent the P(PEGMEMMA) segments.

[00110] **FIG. 9** shows a representative differential scanning calorimetry (DSC) curve obtained from Sample I. There were two glass transition temperatures (T_g) in the DSC profile, at about -50 °C and about +100 °C, corresponding to transition temperatures of P(PEGMEMA) and PPFS blocks, respectively. This result is consistent with microphase phase separation of these blocks in the bulk material.

[00111] Atomic force microscopy (AFM) height images and TEM images of films formed from Sample I were also obtained. For AFM, the film was prepared by spin coating THF solution of Sample I on a cleaned cover glass (for microscopic slide, with dimensions 22mm x 22mm x 0.5 mm). Sample films for TEM were prepared by dipping carbon coated copper grid into a THF solution of Sample I and removing extra solution with a filter paper. Representative AFM and TEM images are shown in **FIGS. 10** and **11** respectively. The AFM and TEM images indicated the formation of nanoscale patterns on the film surface.

[00112] Example IV. Characterization of Sample II, P(PEGMEA)-*b*-PHFBMA

[00113] **FIG. 12** shows representative ^1H NMR spectra of Sample PHFBMA homopolymer and Sample II, which confirmed the chemical structure of Sample II. These spectra were obtained from the samples in CDCl_3 .

[00114] The mono-modal GPC traces shown in **FIG. 13** indicated that Sample II contains a well-defined block copolymer. The molecular weight of Sample II ranged from about 20,000 g/mol to 85,000 g/mol and the PDI of Sample II was less than 1.3.

[00115] Example V.

[00116] Coatings with nano-patterned surfaces were formed from Samples I and II on substrates.

[00117] The coating solutions were prepared by dissolving the respective sample copolymer in either chloroform or tetrahydrofuran, with copolymer concentrations ranging from 5 to 20 mg/mL.

[00118] The coating solutions were deposited on the substrate by either spin coating or dip-coating. The coated liquid layers were dried and cured at elevated temperatures, from about 110 to about 120 °C to obtain topographically and morphologically heterogeneous nano-patterned surfaces.

[00119] The resulting coating showed phase-segregated heterogeneous amphiphilic surfaces.

[00120] The resulting surfaces also showed patterned micro-topography. When the solvent in the coating solution was organic (non-polar), the protrusions on the surface were apparently rich in fluorinated segments. The lower regions were dominated by P(PEGMEA) segments. Upon water treatment, segments rearranged and the topography was reversed.

[00121] **FIGS. 14** and **15** show representative AFM images of a sample coating surface before and after water treatment respectively.

[00122] Example VI.

[00123] Absorption of three different proteins on coatings formed of Sample I, P(PEGMA)-*b*-PPFS, and Sample II, P(PEGMEA)-*b*-PHFBMA, respectively, was tested.

[00124] A quartz crystal microbalance (QCM) with dissipation monitoring (QCM-D) procedure was used to evaluate the adsorption of the three different proteins on sample coating surfaces.

[00125] The procedure of coating/film preparation for QCM is illustrated in **FIG. 16**. Prior to each QCM-D run, the gold sensor surface on the quartz crystals was cleaned in the UV/ozone chamber for 10 minutes and subsequently rinsed thoroughly with deionized water and dried with nitrogen gas. Next, 2mM of mercapto-1-undecanol prepared in ethanol was dropped onto the gold surface and was left to dry overnight in the fume hood. Mercapto-1-undecanol adsorbs spontaneously onto gold surfaces forming a uniform and active -OH terminated monolayer. The two block copolymers, each with concentration of 10 mg/ml

prepared in THF solution were then spin coated onto individual treated gold surfaces.

[00126] Control surfaces used included: a) Hydrophilic surface comprising pure gold surface with the -OH terminated monolayer and without any polymer coating, and b) hydrophobic surface consisting of trimethylsilane chloride deposited onto the treated gold surface and without any polymer coating.

[00127] All surfaces were left to dry overnight and cured for 1 hour at 60 °C the next day before being mounted in the QCM-D measuring chamber. The tests were initiated by first establishing a stable baseline using the background solution (10 mM PBS). When this was achieved, a protein solution (protein concentration 0.5 mg/ml) prepared in 10 mM PBS solution was injected through the measuring cell. Adsorption of protein onto the surfaces was monitored for at least 1 hour and the measuring chamber was then rinsed twice with 5 mL of 10 mM PBS to monitor the desorption of protein (if any) from the polymer surface for a period of 20 minutes.

[00128] The adsorbed mass of protein, Δm , was calculated using the Sauerbrey equation as $\Delta m = C (\Delta f)/n$, where Δf was the change in the frequency of the crystal due to adsorbed mass, n was 3 for these tests, C was a constant ($C=0.177 \text{ mg m}^{-2}\text{Hz}^{-1}$) in the used device).

[00129] The adsorbed mass and dissipation as a function of time of three different proteins, bovine serum albumin (BSA), lipopolysaccharide (LP) from *E. Coli*, and lectin from *Codium Fragile* were measured. Representative results are shown in **FIGS. 17** (BSA) **18** (LP), and **19** (lectin), respectively. Neither the Sauerbrey mass nor the dissipation for all three sample proteins remained stable within 1 hour on coated surfaces (except the pure gold surface). These data suggested that complex structural rearrangement and conformational changes occurred within the polymeric layer. The test results are also listed in **Table I**.

Table I

POLYMER FILM	% Adsorption of Protein		
	BSA	LP	Lectin
Sample I (P(PEGMEMA)- <i>b</i> -PPFS)	23	46	22
Sample II (P(PEGMEA)- <i>b</i> -PHFBMA)	21	55	25
Pure Gold	47	153	46
Hydrophobic Gold	100	100	100

[00130] **Table I** shows the percentage of the final mass of each protein adsorbed onto the different coating surfaces after rinsing with 10 mM PBS solution. The mass of each protein adsorbed onto the polymeric film was normalized against the mass of that particular protein adsorbed onto the hydrophobic gold surface and the percentage of protein adsorbed onto the hydrophobic gold surface was set as 100 percent.

[00131] Example VII. Surface wettability of Samples I and II

[00132] Sample I or Sample II was dissolved in chloroform or 1,4-dioxane to form respective coating solutions. The sample solutions (about 1 mL) were spin-coated onto glass cover slips at a rotary speed of 1000 rpm for 1 minute to obtain uniform thin films. The films were then annealed at about 110 °C for 30 minutes and cooled under nitrogen atmosphere.

[00133] Contact angles of the sample films were measured on a Rame-Hart goniometer by placing a drop of water on several places of each surface and measuring the angles of the water drop on the surface on the right and the left side. Measurements of the contact angles are made before and after BSA adsorption onto the respective polymer surfaces. Results are listed in **Table II**. The values listed in **Table II** are averaged of at least 10 measurements. Similar protocols were followed for measurements on the surfaces subjected to protein adsorption assays as described in Example VI.

TABLE II

Surface	Contact Angle (degree)	
	Before BSA Adsorption	AFTER BSA Adsorption
Sample I	67.2 ± 0.6	85.3 ± 0.7
Sample II	74.5 ± 0.5	88.6 ± 0.6
Pure Gold	80.8 ± 0.4	99.6 ± 0.7
Hydrophobic Gold	101.6 ± 0.7	120.0 ± 0.5

[00134] Example VIII

[00135] Samples III and IV were prepared according to the procedure described in Example I, but with different weight ratios of the component segments.

[00136] Sample III had a P(PEGMEMA) block with 12 repeat units and a PPFS block with 114 repeat units, and is denoted as P(PEGMEMA)₁₂-*b*-PPFS₁₁₄. Sample IV had a P(PEGMEMA) with 19 repeat units and a PPFS block with 95 repeat units, and is denoted as P(PEGMEMA)₁₉-*b*-PPFS₉₅.

[00137] Sample block copolymers produced were dispersed in methanol to precipitate any residual PPFS homopolymer. However, no precipitation was observed confirming a highly efficient chain extension reaction. The removal of any unreacted P(PEGMEMA) homopolymer chains was achieved by dispersing the block copolymers in water with stirring for several hours prior to centrifugation at 4000 rpm.

[00138] The refractive indices of Samples III and IV in THF and aqueous solutions were measured using a BI-DNDC differential refractometer at a wavelength of 620 nm affording the refractive index increment (dn/dc) of each solution. The instrument was calibrated primarily with potassium chloride (KCl) in aqueous solution. The dn/dc values were found to be 0.1350 ± 0.010 and 0.1306 ± 0.008 mL/g for Samples III and IV, respectively, in THF. The values in aqueous solutions at 20 °C were 0.1712 ± 0.012 and 0.1625 ± 0.011 mL/g for Samples III and IV respectively, and increased to 0.1835 ± 0.014 for Sample IV at 50 °C.

[00139] A series of block copolymer solutions with concentrations ranging from 10^{-4} to 1.0 mg/mL were prepared by diluting a stock solution of block copolymer with water. The pyrene solution in acetone was transferred to a number of vials, acetone was then evaporated under nitrogen before adding the block copolymer solutions to give a final pyrene concentration of 6.0×10^{-7} M in each vial. After equilibration overnight at ambient temperature, the excitation spectra (300-360 nm) of the solutions were recorded at an emission wavelength of 395 nm with the excitation and emission bandwidths being set at 3 nm. The ratios of the peak intensities at 338 and 333 nm (I_{338}/I_{333}) of the excitation spectra were analyzed as a function of polymer concentration.

[00140] Fluorescence spectroscopy and DLS experiments were used to determine the critical micelle concentration (cmc) of Samples III and IV in aqueous solutions at 25 °C. The polymer concentration at which the ratio of the peak intensities (I_{338}/I_{333}) and scattering intensity increases sharply was defined as the cmc. The cmc value was taken from the intersection of the tangent to the curve at the inflection with the horizontal tangent through the point at the low concentrations. The cmc of copolymers obtained from both fluorescence spectroscopy and DLS experiments are in good agreement. The estimated cmc of Samples III and IV were shown in Table III. The cmc of Sample III was found approximately 20 times lower than the cmc of Sample IV, suggesting that the minimum concentration above which micellization starts in solution, may be dependent on the block lengths of both blocks. It might be hypothesized that longer PPFS block and shorter P(PEGMEMMA) block would favor micellization, promoted by an increase in hydrophobicity.

[00141] Example IX

[00142] Sample III or IV (1 mg) was dissolved in THF (0.5 mL), and the solution was diluted with deionized water (2 mL) (Millipore Alpha-Q purification system equipped with a 0.22 μ m filter). To ascertain the complete evaporation of THF from the solution, the 2.5 and 2 mL volumes which represent the volumes of solution with and without THF, respectively, were marked on the sample vial. The mass of the initial 2.5 mL polymer solution was also measured. Next, the solution

was left to evaporate at room temperature until the volume has dropped to the 2 mL level, and the mass was observed to decrease until it remains constant where the duration taken is approximately 48 h. The drop in the volume and mass of the solution is mainly due to the complete evaporation of THF (0.5 mL of THF was added to dissolve the polymer) as a very minimal amount of water evaporates at room temperature.

[00143] The molar composition of the Sample block copolymers can be calculated by comparing the integration values of signals d and a of PPFS and P(PEGMEMA) blocks from the NMR spectra (See **FIG. 5**). This composition data can then be combined with absolute molecular weight data (M_w) (which may be estimated from the Zimm plots) from the block copolymers to evaluate the degree of polymerization of each block. For detailed discussion of the calculation procedure, see Tan et al., "Synthesis and Self-Assembly of Brush-Type Poly[poly(ethylene glycol)methyl ether methacrylate]-*block*-poly(pentafluorostyrene) Amphiphilic Diblock Copolymers in Aqueous Solution", *Langmuir*, 2010, vol. 26, pp. 2361-2368, the entire contents of which are incorporated herein by reference.

[00144] Some measured and calculated results are shown in **Table III**. Further results may be found in Tan.

TABLE III

Sample	Sample III	Sample IV
M_n , GPC (g/mol)	31000	17500
PDI	1.3	1.3
cmc (mg/mL)	0.01 ± 0.001	0.2 ± 0.015
$M_{w, \text{single}}$, (g/mol)	36000 ± 980	39500 ± 1300
Micelle Radius (nm)	56 ± 1	27 ± 1

[00145] A schematic representation of the expected micelle structure formed in an aqueous solution is shown in **FIG. 20**.

[00146] Samples III and IV were found to have well-defined brush-type structures, and could form generally spherical micelles in aqueous solution. It was

also found that copolymers with longer P(PEGMEME) blocks formed micelles with smaller radius and lower aggregation numbers in solution. The micelles were found to possess a thick hydration layer. With increasing temperature, the aggregation number increased. An increase in temperature also induced the brush-like PEG segments in the corona to dehydrate and shrink, thus the overall radius of the micelles was found to decrease slightly over the same temperature range.

[00147] Example X

[00148] Cleaned glass slides coated with amino-terminated surface and sample polymer films were suspended vertically in individual centrifuge tubes containing filtered seawater. The films of sample copolymers were prepared as discussed above. The area immersed was about 25 mm x 60 mm and three replicates were used. After 24 h incubation in the dark, the barnacles attached to each slide were counted.

[00149] Field test was conducted on the surfaces at the West Coast of Singapore from 27 February 2009 to 27 March 2009. All test samples were recorded by photography once a week.

[00150] Nanostructured surfaces formed by the self-assembly of amphiphilic block copolymers containing fluorinated and PEG segments were obtained and demonstrated to reduce adsorption of different types of protein. The films of sample copolymers were found to be resistant to the settlement of barnacles.

[00151] Further details are reported in Tan et al., "Barnacle repellent nanostructured surfaces formed by the self-assembly of amphiphilic block copolymers", *Polymer Chemistry*, 2010, advance copy available at http://www.rsc.org/delivery/_ArticleLinking/DisplayHTMLArticleforfree.cfm?JournalCode=PY&Year=2010&ManuscriptID=b9py00332k&Iss=Advance_Article, the entire contents of which are incorporated herein by reference.

[00152] When a list of items is given herein with an "or" before the last item, any of the listed items or any suitable combination of the listed items may be selected and used.

[00153] Of course, the above described embodiments are intended to be illustrative only and in no way limiting. The described embodiments are susceptible to many modifications of form, arrangement of parts, details and order of operation. The invention, rather, is intended to encompass all such modification within its scope, as defined by the claims.

WHAT IS CLAIMED IS:

1. An amphiphilic block copolymer for providing an antifouling surface, comprising:
 - a first polymeric block of repeat units and a second polymeric block of repeat units, copolymerized by living radical polymerization;
 - said first block comprising hydrophilic antifouling side chains bonded to a first backbone segment, said first backbone segment having a length of 10 to 200 repeat units, said side chains having an average length of 5 to 23 monomer units, said repeat units in said first block having a polydispersity index of 1.3 or less; and
 - said second block comprising hydrophobic antifouling side groups bonded to a second backbone segment, said second backbone segment having a length of 10 to 200 repeat units.
2. The copolymer of claim 1, wherein said side groups comprise fluorinated groups.
3. The copolymer of claim 1 or claim 2, wherein said side chains comprise poly(ethylene glycol).
4. The copolymer of any one of claims 1 to 3, wherein said copolymer has a backbone segment formed of an acrylate group.
5. The copolymer of any one of claims 1 to 4, wherein said first block comprises poly(ethylene glycol) methylether methacrylate and said second block comprises poly(pentafluorostyrene).
6. The copolymer of any one of claims 1 to 4, wherein said first block comprises poly(ethylene glycol) methylether acrylate and said second block comprises poly(hexafluorobutyl methacrylate).
7. The copolymer of any one of claims 1 to 6, wherein said polydispersity index of said repeat units of said first block is about 1.15.

8. The copolymer of any one of claims 1 to 7, further comprising a third block of repeat units that is different from said first and second block.
9. A composition for providing an antifouling surface, comprising:

an amphiphilic block copolymer comprising a first polymeric block of repeat units and a second polymeric block of repeat units, said first block comprising hydrophilic antifouling side chains bonded to a first backbone segment, said first backbone segment having a length of 10 to 200 repeat units, said side chains having an average length of 5 to 23 monomer units, said repeat units in said first block having a polydispersity index of 1.3 or less, and said second block comprising hydrophobic antifouling side groups bonded to a second backbone segment, said second backbone segment having a length of 10 to 200 repeat units,

wherein said block copolymer in said composition has a polydispersity index of 1.3 or less.
10. The composition of claim 9, wherein said block copolymer is the block copolymer of any one of claims 1 to 8.
11. An antifouling coating comprising the composition of claim 9 or claim 10.
12. The antifouling coating of claim 11, comprising a coating surface having inter-dispersed hydrophobic regions and hydrophilic regions, said hydrophobic regions being formed of said hydrophobic antifouling side groups of said block copolymer, and said hydrophilic regions being formed of said hydrophilic antifouling side chains of said block copolymer.
13. The antifouling coating of claim 12, wherein one of said hydrophobic regions and said hydrophilic regions form a continuous phase and the other of said hydrophobic regions and hydrophilic regions form a dispersed phase.
14. The antifouling coating of claim 13, wherein said dispersed regions have an average size from 1 nanometer to 1 micrometer.
15. The antifouling coating of claim 14, wherein said average size is about 20 nm.

16. A solution comprising a solvent and the composition of claim 9 or claim 10 dispersed in said solvent.
17. A method of forming an antifouling coating from the solution of claim 16, comprising:
- depositing a layer of said solution on a surface;
 - heating said solution to facilitate phase separation in said solution; and
 - removing the solvent from said layer of said solution after said copolymer has phase separated to form separate hydrophilic and hydrophobic phases.
18. A method of forming the block copolymer of any one of claims 1 to 8, comprising:
- obtaining a first precursor for the first block and a second precursor for the second block;
 - copolymerizing said first and second precursors by living radical polymerization, to form said block copolymer.
19. The method of claim 18, wherein said living radical polymerization comprises atom transfer radical polymerization.
20. The method of claim 18, wherein said living radical polymerization comprises reversible addition-fragmentation chain transfer polymerization.
21. The method of any one of claims 18 to 20, wherein said first precursor is a polymer having a polydispersity index of 1.3 or less.
22. The method of any one of claims 18 to 21, wherein said first precursor is formed by living radical polymerization.