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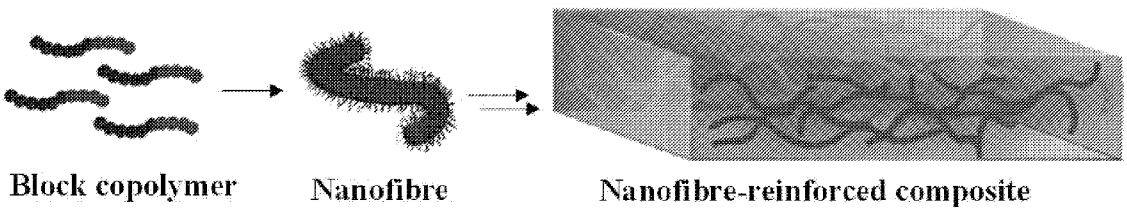

Figure 11

(57) Abstract: The present disclosure relates to the field of synthesis of block copolymers, and polymeric nanofibers having a core-shell morphology produced therefrom. The present disclosure relates to the field of synthesis of block copolymers where one block is more hydrophobic than the other block and is a different composition. The disclosure also relates to uses of these polymeric nanofibers in various applications, such as reinforcing a polymeric matrix and for coatings applications.

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SYNTHESIS OF AMPHIPHILIC BLOCK COPOLYMERS AND POLYMERIC NANOFIBERS PRODUCED THEREFROM

RELATED APPLICATIONS

[0001] This application claims priority from Australian Provisional Patent Application No. 2021903943 filed on 6 December 2021, the entire contents of which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present invention relates to the field of synthesis of block copolymers, and polymeric nanofibers having a core-shell morphology produced therefrom. The invention also relates to uses of these polymeric nanofibers in various applications, such as reinforcing a polymeric matrix and for coatings applications. However, it will be appreciated that the invention is not limited to these particular fields of use.

BACKGROUND OF THE INVENTION

[0003] The following discussion of the prior art is provided to place the invention in an appropriate technical context and enable the advantages of it to be more fully understood. It should be appreciated, however, that any discussion of the prior art throughout the specification should not be considered as an express or implied admission that such prior art is widely known or forms part of the common general knowledge in the field.

[0004] Polymerization-induced self-assembly (PISA) has recently attracted major interest for synthesis of amphiphilic block copolymer nanoparticles with complex morphologies at high solids content (up to 50%). Although PISA can in principle be conducted using any reversible deactivation radical polymerization (RDRP) technique, reversible addition-fragmentation chain transfer (RAFT) mediated PISA is by far the most commonly used method. It is noteworthy that PISA can also be performed using addition-fragmentation chain transfer (AFCT) polymerization, *i.e.* a "non-living" polymerization technique. RAFT PISA can be implemented both as a dispersion polymerization and aqueous emulsion polymerization.

[0005] In RAFT-mediated PISA, a solvophilic macroRAFT agent is chain extended with solvophobic core-forming monomer(s). As the polymerization proceeds, the increasing insolubility of the core-forming block drives *in-situ* self-assembly resulting in block copolymer nanoparticles. The morphology is determined by a number of factors, but can largely be

rationalized based on the relative molecular weights of the solvophilic block (i.e., the "corona" or shell-forming block) and the solvophobic block (core-forming block). The morphologies typically change from spheres, fibers and vesicles with increasing length of the solvophobic block.

[0006] Polymeric materials are ubiquitous in today's society. It is a common strategy, and often a requirement, to employ various so-called fillers (additives) to tune and improve polymeric material performance. However, traditionally employed fillers, e.g., carbon black and glass fibers, are associated with significant disadvantages such as high density of the final reinforced polymeric material, the requirement for a relatively high weight fraction of filler, and/or lack of transparency. In addition, traditional fillers tend to only offer limited material improvements in terms of a high fracture strain and stretchability. Furthermore, current fillers are typically difficult to disperse in a polymer matrix and surface modification is typically required, adding cost to the process.

[0007] The prior art teaches the use of high T_g core-forming blocks in amphiphilic block copolymers, and the formation of nanofibers prepared by PISA in RAFT aqueous emulsion polymerization. Conventional wisdom is that a 'hard' core is required to form a nanofiber and also to provide mechanical properties as a filler. In particular, PISA has been conducted using a second block (core-forming block) of high T_g monomers such as styrene ($T_g \approx 100$ °C), methyl methacrylate (MMA) ($T_g \approx 105$ °C), and 2-hydroxypropyl methacrylate (HPMA) ($T_g \approx 72$ °C). In other studies, only lower-order spherical morphologies resulted from the use of a low T_g core-forming block in aqueous emulsion RAFT PISA. These include copolymers which are formed by statistical copolymerization of MMA and *n*-butyl acrylate (*n*BA), homopolymerization of *n*BA ($T_g \approx -54$ °C) and benzyl methacrylate (BzMA) ($T_g \approx 54$ °C), and copolymerization of *n*BA and MMA with poly(ethylene oxide) macroRAFT agent. In addition to these studies, there are reports of copolymers of poly(acrylic acid)-*b*-poly(*n*BA) diblock copolymer nanoparticles, poly(glycerol monomethacrylate)-poly(BzMA) diblock copolymer, poly(2-(diethylamino)ethyl methacrylate)-poly(methacrylic acid-*stat*-BzMA) and poly(acrylic acid)-*b*-poly(*n*BA)-*co*-poly(styrene) triblock copolymer nanoparticles. However, in all of the above studies, only spherical nanoparticles were obtained.

[0008] It is an object of the present invention to overcome or ameliorate one or more of the disadvantages of the prior art, or at least to provide a useful alternative.

SUMMARY OF INVENTION

[0009] The syntheses of self-assembled nanofibers formed via a RAFT-PISA process have been disclosed herein. In particular, in one form of the invention amphiphilic block copolymers are disclosed wherein the core is a copolymer that has a Tg of about 75°C (and lower). In another form of the invention, amphiphilic block copolymers are disclosed wherein the core is a homopolymer and has a Tg of about 16°C (and lower). In another form of the invention, nanofibers are disclosed wherein the core is a copolymer or a homopolymer having a Tg up to 16°C. Additionally, in a further form of the invention, block copolymers are disclosed wherein the core and the shell are prepared from a hydrophobic copolymer or homopolymer.

[0010] The present invention is a significant advance over the prior art. The inventive copolymers disclosed herein can efficiently self-assemble to form stable nanofibers in high concentrations that can be used in a variety of applications. The present invention provides one or more of the following advantages: composites including the nanofiber of the invention that are tougher and/or have higher impact resistance; lower density composite materials comprising the nanofiber of the invention; nanofiber reinforced composites which have higher stiffness and are relatively lighter (of the order of about 10-20% weight reduction, which is a significant reduction; in some embodiments, the weight reduction is 5-40%); nanofiber reinforced composites which display higher elongation at break; nanofiber reinforced composites that are substantially transparent through matching refractive indices of the inventive nanofibers disclosed herein with the polymer matrix into which they are dispersed; and/or an improved control of rheological properties (thixotropy) of emulsions by use of the nanofibers of the invention. Additionally, as mentioned above, current fillers for composites can be difficult to disperse in a polymer matrix and surface modification is typically required, adding cost to the process. However, the nanofibers of the invention do not require surface modifications as the external surface, or shell, is solvophilic and can be wetted by polar polymers, solvents or other matrix, and they can relatively easily disperse in a polymer matrix. Furthermore, it is possible to prepare surface coatings and films that are substantially or completely formed from the nanofibers of the invention.

[0011] According to a **first** aspect, the present invention provides a polymeric nanofiber having a core-shell morphology, wherein the shell is hydrophilic, and the core comprises:

a) a hydrophobic copolymer, or

b) a hydrophobic homopolymer having a Tg below 16°C.

[0012] According to a **second** aspect, the present invention provides an amphiphilic block copolymer comprising:

a block [A] comprising a hydrophilic homo- or copolymer; and

a block [B] comprising:

a) a hydrophobic copolymer having a Tg below about 75°C, or

b) a hydrophobic homopolymer having a Tg below about 16°C;

and optionally a crosslinker.

[0013] In preferred embodiments of the first and second aspects of the invention, the hydrophobic homopolymer has a Tg in the range of about -70°C and up to 16°C or about 16°C. In preferred embodiments of the first and second aspects of the invention, the hydrophobic copolymer has a Tg in the range of about -70°C to about 75°C.

[0014] According to a **third** aspect, the present invention provides a method of producing the amphiphilic block copolymer of the second aspect, the method comprising the steps of:

a) reacting at least one hydrophilic monomer using RDRP to form a hydrophilic block [A];

b) adding to hydrophilic block [A], a hydrophobic block [B] comprising at least one hydrophobic monomer using RDRP; and

c) optionally adding a crosslinker at step b).

[0015] According to a **fourth** aspect, the present invention provides a nanofiber when self-assembled from the amphiphilic block copolymer produced by the method of the third aspect.

[0016] According to a **fifth** aspect, the present invention provides the use of the nanofiber of the first or fourth aspects to at least partially produce a film or coating.

[0017] According to a **sixth** aspect, the present invention provides a method of forming the film or coating of the fifth aspect, the method comprising the steps of:

dispersing the nanofiber of the first or fourth aspects in a solvent to form a dispersion;

applying the dispersion to a surface; and

allowing or causing the solvent to substantially or completely evaporate, thereby forming said film.

[0018] According to a **seventh** aspect, the present invention provides the use of the nanofiber of the first or fourth aspects to prepare a composite material, comprising:

a matrix or binder; and

a nanofiber of the first or fourth aspects dispersed throughout the matrix or binder.

[0019] According to an **eighth** aspect, the present invention provides the use of the nanofiber of the first or fourth aspects to modify or improve the mechanical properties of a matrix or binder.

[0020] According to a **ninth** aspect, the present invention provides a method of producing a composite material, the method comprising the steps of:

providing a polymer dispersion;

dispersing the nanofiber of the first or fourth aspects in said polymer dispersion to form a mixture; and

drying the mixture so as to form the composite material.

[0021] According to a **tenth** aspect, the present invention provides a method of producing a composite material comprising a polymer and the nanofiber of the first or fourth aspects by melt extrusion, the method comprising the steps of:

heating a polymer and the nanofiber to a temperature greater than a melt temperature of the polymer;

mixing the polymer and the nanofiber; and

extruding the mixture to form the composite material.

[0022] According to an **eleventh** aspect, the present invention provides the use of a polymeric nanofiber as a viscosity or rheology modifier, wherein the polymeric nanofiber comprises a core-shell morphology, wherein the shell is hydrophilic, and the core comprises a hydrophobic homopolymer or copolymer.

[0023] According to a **twelfth** aspect, the present invention provides the use of a polymeric

nanofiber according to the first or fourth aspects as a viscosity or rheology modifier.

[0024] According to a **thirteenth** aspect, the present invention provides the method of producing a block copolymer, the method comprising the steps of:

a) reacting at least one hydrophobic monomer using RDRP to form a substantially hydrophobic block [A], wherein block [A] is substantially soluble in an 20/80 vol% water/ethanol mixture;

b) adding to hydrophobic block [A], a hydrophobic block [B] comprising at least one hydrophobic monomer using RDRP in the presence of at least one polar solvent, wherein block [B] is more hydrophobic than block [A] and is a different composition to block [A]; and

c) optionally adding a crosslinker at step b).

[0025] The block copolymer produced according to the thirteenth aspect may self-assemble into a nanofiber having a core-shell morphology.

[0026] In a preferred embodiment of the thirteenth aspect, block [A] is substantially insoluble in water.

[0027] The nanofibers of the present invention are formed from polymers. The monomeric units may be of a single type (homopolymer), or a variety of types (copolymer). The physical behaviour of the polymer is dictated by several features, including the total molecular weight, the composition of the polymer (e.g., the relative concentrations of different monomers), the chemical identity of each monomeric unit and its interaction with a solvent, and the architecture of the polymer (e.g., whether it is single chain or branched chains).

[0028] In one aspect, the present invention provides a process for preparing amphiphilic block copolymers comprising blocks [A] and [B],

wherein block [A] is a hydrophilic homo- or copolymer, and

wherein block [B] is a hydrophobic homopolymer having a Tg below 16°C or about 16°C, or a hydrophobic copolymer having a Tg of the hydrophobic block below about 75°C,

wherein the process comprises obtaining blocks [A] and [B] by RDRP, preferably via RAFT of ethylenically unsaturated monomers, and

optionally comprising a crosslinker.

[0029] In another aspect, the present invention provides a process for preparing block copolymers comprising blocks [A] and [B],

wherein block [A] is a hydrophobic homo- or copolymer, and

wherein block [B] is a hydrophobic homo- or copolymer,

wherein the process comprises obtaining blocks [A] and [B] by RDRP, preferably via RAFT of ethylenically unsaturated monomers, and

optionally comprising a crosslinker.

[0030] It will be appreciated that the block copolymers of the present invention self-assemble into a nanofiber.

[0031] According to a **fourteenth** aspect, the present invention provides a block copolymer comprising: a hydrophobic block [A], wherein block [A] is substantially soluble in an 20/80 vol.% water / ethanol mixture; and a hydrophobic block [B] comprising at least one hydrophobic monomer, wherein block [B] is more hydrophobic than block [A] and is a different composition to block [A]; and optionally a crosslinker.

[0032] According to a **fifteenth** aspect, the present invention provides a polymeric nanofiber having a core-shell morphology, wherein the shell is hydrophobic, and the shell comprises a polymer that is substantially soluble in an 20/80 vol.% water / ethanol mixture; and wherein the core is hydrophobic, and the core comprises a polymer that is more hydrophobic than the polymer of the shell, and is a different composition to the polymer of the shell.

[0033] Use of the block copolymer of the fourteenth aspect or the polymeric nanofiber of the fifteenth aspect to at least partially produce a film or coating.

[0034] Use of the block copolymer of the fourteenth aspect or the polymeric nanofiber of the fifteenth aspect to prepare a composite material, comprising: a matrix or binder; and a block copolymer of the fourteenth aspect or the polymeric nanofiber of the fifteenth aspect dispersed throughout the matrix or binder.

[0035] Use of the block copolymer of the fourteenth aspect or the polymeric nanofiber of the fifteenth aspect to modify or improve the mechanical properties of a matrix or binder

[0036] Use of the block copolymer of the fourteenth aspect or the polymeric nanofiber of the fifteenth aspect as a viscosity or rheology modifier.

RAFT polymerization

[0037] RAFT polymerization is one of the most robust and versatile methods for providing living characteristics to radical polymerization. With appropriate selection of the chain transfer agent (RAFT agent) for the monomers and reaction conditions, it is applicable to the majority of monomers subject to radical polymerization. The process can be used in the synthesis of well-defined homo-, gradient, diblock, triblock, and star polymers and more complex architectures, which include microgels and polymer brushes.

[0038] When preparing, for example, a block copolymer in the presence of the chain transfer agent (RAFT agent), the end of the growing block is provided with a specific functionality that controls the growth of the block by means of RDRP. The functionality at the end of the block is of such a nature that it can reactivate the growth of the block in a second and/or third stage of the polymerization process with other ethylenically unsaturated monomers providing a covalent bond between, for example, a first and second block [A] and [B] and with any further optional blocks.

[0039] Further details on the chemistry of synthesis of block copolymers by RAFT processes can be found in the following publications, each of which is herein incorporated in its entirety by reference: *Polymer*, 2008, volume 49, 1079-1131; *Chemical Society Reviews*, 2014, volume 43, 496-505; *Macromolecules*, 1998, volume 31, 5559-5562; and *Polymer*, 2013, volume 54, 2011-2019.

[0040] In one non-limiting embodiment, the block copolymer according to the disclosed and/or claimed inventive concepts is obtained by RAFT polymerization.

Radical Initiators

[0041] The radical initiator is chosen to have an appropriate half-life at the temperature of polymerization sufficient to initiate polymerization.

[0042] Non-limiting examples of radical initiators suitable for the invention include one or more of the following compounds: 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-cyanobutane), dimethyl 2,2'-azobis(isobutyrate), 4,4'-azobis(4-cyanovaleric acid), 4,4'-azobis-(4-cyanopentanoic acid), 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, 1, 1 '-

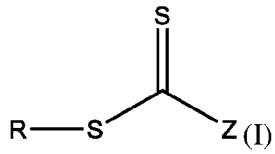
azobis(cyclohexanecarbonitrile), 2-(t-butylazo)-2-cyanopropane, 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramidine), 2,2'-azobis{2- methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, 2,2'-azobis{2-methyl-N-[1, 1-bis(hydroxymethyl)-2-ethyl]propionamide}, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(isobutyramide) dihydrate, 2,2'-azobis(2,2,4-trimethylpentane), 2,2'-azobis(2-methylpropane), t-butyl peroxyacetate, t-butyl peroxybenzoate, t-butyl peroxyneodecanoate, t-butylperoxy isobutyrate, t-amyl peroxypivalate, t-butyl peroxypivalate, diisopropyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, dicumyl peroxide, dibenzoyl peroxide, dilauroyl peroxide, potassium peroxydisulfate, ammonium peroxydisulfate, di-t-butyl hyponitrite, dicumyl hyponitrite, and the like. Other suitable initiating systems are described in texts. See, for example, Moad and Solomon "the Chemistry of Free Radical Polymerization", Pergamon, London, 1995, pp 53-95.

[0043] In one embodiment, the radical initiator is 4,4'-azobis-(4-cyanopentanoic acid).

Chain Transfer Agents

[0044] The chain transfer agent is generally selected having regard to the type of monomers that are to be polymerized. Suitable chain transfer agents for use with the present invention include chain transfer agents for RDRP including, nitroxide-mediated radical polymerization (NMP), atom-transfer radical polymerization (ATRP), and RAFT. Other chain transfer agents will be known to the skilled person.

[0045] Examples of chain transfer agents compatible with the invention have a structure of (I)



(I)

wherein Z is group which enhances the reactivity of the C=S moiety

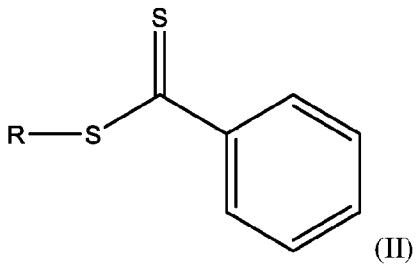
wherein R is a homoloytic leaving group capable of initiating radical polymerization.

[0046] In an embodiment of the invention, R is selected from the group consisting of secondary cyanoalkyls such as cyanomethyl, 1-cyanoethyl, 2-cyanopropan-2-yl, primary and

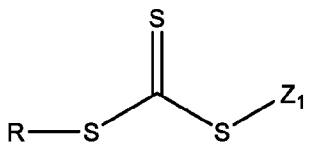
secondary alkoxylcarbonylalkyls such as ethoxycarbonylmethyl, 1- ethoxycarbonylethyl and primary and secondary carboxyalkyls, tertiary cyanoalkyls such as 2-cyanobutan-2-yl, 1-cyanocyclohexyl, 2-cyano-4-methylpentan-2-yl, 2-cyano-4- methoxy-4-methylpentan-2-yl, 2-cyano-4-carboxybutan-2-yl, 2-cyano-5-hydroxypentan-2-yl, secondary cyano(aryl)alkyls such as cyano(phenyl)methyl, tertiary alkoxylcarbonylalkyls such as 2-alkoxycarbonylpropan-2-yl, 1-(butylamino)-2-methyl-l-oxopropan-2-yl, tertiary carboxyalkyls, secondary aryl(alkoxylcarbonyl)alkyls such as phenyl(ethoxycarbonyl)methyl, and other tertiary radicals such as 1-(cyclohexylamino)-2- methyl-l-oxopropan-2-yl, 1-(2-hydroxyethylamino)-2-methyl-l-oxopropan-2-yl, 1-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-ylamino)-2-methyl-l-oxopropan-2-yl, 2-(4,5-dihydro-l H-imidazol-2-yl)propan-2-yl, and 2-(1-(2-hydroxyethyl)-4,5-dihydro-lHimidazol-2-yl)propan-2-yl; and

Z is selected from the group consisting of aryl, C_{1-30} alkyl, -S-C alkyl, -O-aryl, -N(C_{1-6} alkyl)$_2$, -N(aryl)(C_{1-6} alkyl), -heteroaryl, -heterocyclyl, -OC_{1-30} alkyl, heterocyclyl, and phosphate, wherein each of -aryl, -C_{1-30} alkyl, -heteroaryl, and - heterocyclyl may be optionally substituted from 1 to 4 times with a substituent independently selected from the group consisting of C_{1-30} alkyl, =O, -CN, aryl, and -COOC_{1-6} alkyl.

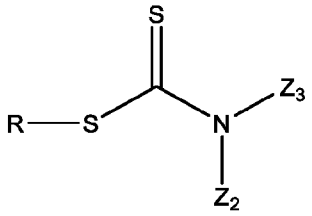
[0047] In other embodiments of the invention, the chain transfer agent has a structure of (II), (III), or (IV)



(II)



(III)



(IV)

wherein R, Z_1, Z_2, and Z_3 are as defined in Formula (I).

[0048] In an embodiment, the chain transfer agent is a RAFT agent.

[0049] In a non-limiting embodiment, the chain transfer agents can be one or more compounds selected from the group consisting of dithiobenzoates, dithioesters, thioethers-thiones, trithiocarbonates, dithiocarbamates, xanthates and mixtures thereof.

[0050] In one embodiment, the RAFT agent is a macroRAFT agent.

[0051] As used herein, the term "macroRAFT" or "macroRAFT agent" means a RAFT agent which comprises one or more monomers.

[0052] In certain embodiments, the macroRAFT agent is prepared by a method comprising polymerizing one or more unsaturated monomers under the control of a RAFT agent to form a macroRAFT agent.

[0053] In one embodiment, the macroRAFT agent is of the general formula (block [A])-RAFT, wherein block [A] is a hydrophilic polymer or copolymer as defined herein, and RAFT is a RAFT agent as described herein. In other words, the macroRAFT agent consists of a RAFT agent bound to a hydrophilic block of the present invention.

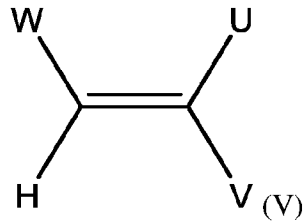
[0054] In one embodiment, the macroRAFT agent is P(AA-*stat*-PEGA)-DDMAT.

[0055] In another embodiment, the macroRAFT agent is P(AA-*stat*-PEGA)-TTC.

Monomers

[0056] Suitable polymers for the present invention include those that are prepared by any polymerization process. If desired, the monomers should also be capable of being polymerized with other monomers (*e.g.,* a copolymer). The factors which determine copolymerizability of various monomers are well documented in the art. For example, see: Greenlee, R.Z., in Polymer Handbook 4th Edition (Brandup, J., and Immergut. E.H., Grulke, E.A., John Wiley & Sons Ltd., Hoboken, 1999).

[0057] Suitable monomers that may be used in accordance with the invention include those of formula (V):



(V)

where U and W are independently selected from $-CO_2H$, $-CO_2R^1$, $-COR^1$, $-CSR^1$, $-CSOR^1$, $-COSR^1$, $-CONH_2$, $-CONHR^1$, $-CONR^1{}_2$, hydrogen, halogen and optionally substituted C_1-C_4 alkyl or U and W form together a lactone, anhydride or imide ring that may itself be optionally substituted, where the optional substituents are independently selected from hydroxy, $-CO_2H$, $-CO_2R^1$, $-COR^1$, $-CSR^1$, $-CSOR^1$,$-COSR^1$,-CN, $-CONH_2$, $-CONHR^1$, $-CONR^1{}_2$, $-OR^1$, $-SR^1$, $-O_2CR^1$, $-SCOR^1$, and $OCSR^1$; and

where V is selected from hydrogen; R^1, $-CO_2H$, $-CO_2R^1$, $-COR^1$, $-CSR^1$, $-CSOR^1$, $COSR^1$, $-CONH_2$, $-CONHR^1$, $-CONR^1{}_2$, $-OR^1$, $-SR^1$, $-O_2CR^1$, $-SCOR^1$, and $-OCSR^1$;

where each R^1 is independently selected from optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, optionally substituted aryl, optionally substituted heteroaryl, optionally substituted carbocyclyl, optionally substituted heterocyclyl, optionally substituted arylalkyl, optionally substituted heteroarylalkyl, optionally substituted alkylaryl, optionally substituted alkylheteroaryl, and an optionally substituted polymer chain.

[0058] Examples of optional substituents for R^1 include those selected from alkyleneoxidyl (epoxy), hydroxy, alkoxy, acyl, alkylcarbonyl, carboxy, sulfonic acid, isocyanato, cyano, silyl, halo, amino, including salts and derivatives thereof.

[0059] Examples of polymer chains include those selected from polyalkylene oxide, polyarylene ether and polyalkylene ether.

[0060] Non-limiting examples of monomers include maleic anhydride, N-alkylmaleimide, Narylmaleimide, dialkyl fumarate and cyclopolymerizable monomers, acrylate and methacrylate esters, acrylic and methacrylic acid, styrene, acrylamide, methacrylamide, and methacrylonitrile, mixtures of these monomers, methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2- ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene, methyl acrylate, ethyl acrylate, propyl acrylate (all isomers), butyl acrylate (all isomers e.g., n-butyl acrylate), 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylates, acrylates selected from

glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate (all isomers), hydroxybutyl methacrylate (all isomers), N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate (all isomers), hydroxybutyl acrylate (all isomers), N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,Ndimethylacrylamide, N-tert-butylmethacrylamide, N-n-butyl methacrylamide, N-methylolmethacrylamide, N-ethylolmethacrylamide, N-tert-butylacrylamide, N-nbutylacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid (all isomers), diethylamino styrene (all isomers), alpha-methylvinyl benzoic acid (all isomers), diethylamino alpha-methylstyrene (all isomers), p-vinylbenzene sulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethylsilylpropyl methacrylate, dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilyl propyl acrylate, tributoxysilyl propyl acrylate, dimethoxymethylsilyl propyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, ethylene and chloroprene, and the like.

[0061] Non-limiting examples of acrylate monomers include methyl acrylate, methyl alpha-bromoacrylate, methyl 2-(bromomethyl)acrylate, methyl 2-(chloromethyl)acrylate, methyl 2-(trifluoromethyl)acrylate, ethyl acrylate, 2-(2-ethoxyethoxy)ethyl acrylate, 2-phenoxyethyl acrylate, alkoxylated phenol acrylates, alkoxylated tetrahydrofurfuryl acrylates, dicyclopentadienyl acrylate, 3,3,5-trimethylcyclohexyl acrylate, ethoxylated hydroxyethyl acrylates, ethoxylated nonyl phenol acrylates, methoxy polyethylene glycol acrylates, polypropylene glycol acrylates, triethylene glycol ethyl ether acrylate, ethyl 2-(bromomethyl)acrylate, ethyl cis-(beta-cyano)acrylate, 2-ethylhexyl 2-cyano-3,3-diphenylacrylate, diacetone acrylate, mono-2-acryloyloxyalkyl succinate, mono-2-acryloyloxyethyl succinate, mono-2-acryloyloxyalkyl phthalate, mono-2-acryloyloxyethyl phthalate, ethylene glycol dicyclopentenyl ether acrylate, ethylene glycol methyl ether acrylate,

ethylene glycol phenyl ether acrylate, ethyl 2-ethylacrylate, 2-ethylhexyl acrylate, ethyl 2-propylacrylate, 4-acetoxyphenethyl acrylate, [2-(acryloyloxy)ethyl]trimethylammonium chloride, 2-(4-benzoyl-3-hydroxyphenoxy)ethyl acrylate, benzyl 2-propylacrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, tert-butyl acrylate, tert-butyl 2-bromoacrylate, 4-tertbutylcyclohexyl acrylate, 2-carboxyethyl acrylate, 2-chloroethyl acrylate, di(ethylene glycol) ethyl ether acrylate, di(ethylene glycol) 2-ethylhexyl ether acrylate, cyclohexyl acrylate, n-pentylacrylate, n-hexyl acrylate, cyclohexyl acrylate, 4-hydroxybutyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxy-3-phenoxypropyl acrylate, hydroxypropyl acrylate, benzyl acrylate, phenethyl acrylate, isobornyl acrylate, isooctyl acrylate, tert-octyl acrylate, n-decyl acrylate, isodecyl acrylate, undecyl acrylate, 10-undecenyl acrylate, dodecyl acrylate, lauryl acrylate, myristyl acrylate, stearyl acrylate, palmityl acrylate, octadecyl acrylate, n-eicosyl acrylate, isonorbornyl acrylate, pentabromobenzyl acrylate, pentabromophenyl acrylate, pentafluorophenyl acrylate, poly(ethylene glycol) methyl ether acrylate, poly(propylene glycol) acrylate, tetrahydrofurfuryl acrylate, 3,5,5-trimethylhexyl acrylate, acetonyl acrylate, 2-carboxyethyl acrylate, carboxymethyl acrylate, oxazolidinylethyl acrylate, methoxyethoxyethyl acrylate, cyclohexyloxymethyl acrylate, methoxymethoxyethyl acrylate, benzyloxymethyl acrylate, 2-butoxyethyl acrylate, 2-ethoxyethoxymethyl acrylate, 2-ethoxyethyl acrylate, allyloxymethyl acrylate, 2,3-dibromopropyl acrylate, 4-bromophenyl acrylate, 1,3-dichloro-2-propyl acrylate, 2-bromoethyl acrylate, 2-iodoethyl acrylate, chloromethyl acrylate, 2-isocyanatoethyl acrylate, 2-acetoacetoxyethyl acrylate, dialkylaminoalkyl acrylates such as 2-(dimethylamino)ethyl acrylate, 2-(diethylamino)ethyl acrylate, 3-(dimethylamino)propyl acrylate, 3-(diethylamino)propyl acrylate, and the like; quaternary ammonium salts of dialkylaminoalkyl acrylates such as, for example, acryloyloxyethyl trimethyl ammonium chloride, acryloyloxypropyl trimethyl ammonium chloride, acryloyloxypropyl lauryl dimethyl ammonium chloride, acryloyloxyethyl ethyl dimethyl ammonium ethylsulfate, acryloyloxyethyl trimethyl ammonium sulfate, and acryloyloxyethyl trimethyl ammonium methosulfate, phosphorus-containing acrylates such as diethyl[(acryloyloxy)methyl]phosphonate, diethyl[(acryloyloxy)ethyl]phosphonate, diethyl(acryloyloxy)methyl phosphate, and diethyl(acryloyloxy)ethyl phosphate, sulfur-containing acrylates like 4-thiocyanatobutyl acrylate, thiocyanathomethyl acrylate, 2-methylthioethyl acrylate, 2-methylsulfonylethyl acrylate, 2-ethylthioethyl acrylate, 2-ethylsulfonylethyl acrylate, 2-propylthioethyl acrylate, 4-methylthiobutyl acrylate, 2,3-bis(methylthio)propyl acrylate, 2,3-bis(methylsulfonyl)propyl acrylate, 2,3-bis(ethylthio)propyl acrylate, 2,3-bis(butylsulfonyl)propyl acrylate, and 2-methylthio-3-ethylthiopropyl acrylate, silicon-containing acrylates such as 2-(trimethylsilyloxy)ethyl acrylate, trimethylsilylmethyl

acrylate, diphenylmethylsilylmethyl acrylate, ethyl 2-(trimethylsilylmethyl)acrylate, 3-[tris(trimethylsiloxy)silyl]propyl acrylate, and 3-(trimethoxysilyl)propyl acrylate, methyl methacrylate, methyl alpha-bromomethacrylate, methyl 2-(bromomethyl)methacrylate, methyl 2-(chloromethyl)methacrylate, methyl 2-(trifluoromethyl)methacrylate, ethyl methacrylate, 2-(2-ethoxyethoxy)ethyl methacrylate, 2-phenoxyethyl methacrylate, alkoxylated phenol methacrylates, alkoxylated tetrahydrofurfuryl methacrylates, dicyclopentadienyl methacrylate, 3,3,5-trimethylcyclohexyl methacrylate, ethoxylated hydroxyethyl methacrylates, ethoxylated nonyl phenol methacrylates, methoxy polyethylene glycol methacrylates, polypropylene glycol methacrylates, triethylene glycol ethyl ether methacrylate, ethyl 2-(bromomethyl)methacrylate, ethyl cis-(beta-cyano)methacrylate, 2-ethylhexyl 2-cyano-3,3-diphenylmethacrylate, diacetone methacrylate, mono-2-methacryloyloxyethylsuccinate, mono-2-methacryloyloxyalkyl succinate, mono-2-methacryloyloxyethyl phthalate, mono-2-methacryloyloxyalkyl phthalate, ethylene glycol dicyclopentenyl ether methacrylate, ethylene glycol methyl ether methacrylate, ethylene glycol phenyl ether methacrylate, ethyl 2-ethylmethacrylate, 2-ethylhexyl methacrylate, ethyl 2-propylmethacrylate, 4-acetoxyphenethyl methacrylate, [2-(methacryloyloxy)ethyl] trimethylammonium chloride, 2-(4-benzoy 1-3-hydroxyphenoxy)ethylmethacrylate, benzyl 2-propylmethacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, tert-butyl methacrylate, tertbutyl 2-bromomethacrylate, 4-tert-butylcyclohexyl methacrylate, 2-carboxyethyl methacrylate, 2-chloroethyl methacrylate, di(ethylene glycol) ethyl ether methacrylate, di(ethylene glycol) 2-ethylhexyl ether methacrylate, cyclohexyl methacrylate, dialkylaminoalkylene methacrylates such as, for example, 2-(dimethylamino)ethylmethacrylate, 2-(diethylamino)ethylmethacrylate, 3-(dimethylamino)propylmethacrylate, and 3-(diethylamino)propyl methacrylate, quaternary ammonium salts of dialkylaminoalkylene methacrylates such as, for example, methacryloyloxyethyl trimethyl ammonium chloride, methacryloyloxypropyl trimethyl ammonium chloride, methacryloyloxypropyl lauryl dimethyl ammonium chloride, methacryloyloxyethyl ethyl dimethyl ammonium ethylsulfate, methacryloyloxyethyl trimethyl ammonium sulfate, and methacryloyloxyethyl trimethyl ammonium methosulfate, n-pentyl methacrylate, n-hexyl methacrylate, cyclohexyl methacrylate, 4-hydroxybutyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxy-3-phenoxypropyl methacrylate, hydroxypropyl methacrylate, benzyl methacrylate, phenethyl methacrylate, isobornyl methacrylate, isooctyl methacrylate, tert-octyl methacrylate, n-decyl methacrylate, isodecyl methacrylate, undecyl methacrylate, 10-undecenyl methacrylate, dodecyl methacrylate, lauryl methacrylate, myristyl methacrylate, stearyl methacrylate, palmityl methacrylate, octadecyl methacrylate, n-eicosyl methacrylate, iso-norbornyl methacrylate, pentabromobenzyl methacrylate, pentabromophenyl

methacrylate, pentafluorophenyl methacrylate, poly(ethylene glycol) methyl ether methacrylate, poly(propylene glycol) methacrylate, tetrahydrofurfuryl methacrylate, ethyl 2-(trimethylsilylmethyl)methacrylate, 3,5,5-trimethylhexyl methacrylate, acetonyl methacrylate, 2-carboxyethyl methacrylate, carboxymethyl methacrylate, oxazolidinylethyl methacrylate, methoxyethoxyethyl methacrylate, cyclohexyloxymethyl methacrylate, methoxymethoxyethyl methacrylate, bezyloxymethyl methacrylate, 2-butoxyethyl methacrylate, 2-ethoxyethoxymethyl methacrylate, 2-ethoxyethyl methacrylate, allyloxymethyl methacrylate,2,3-dibromopropyl methacrylate, 4-bromophenyl methacrylate, 1,3-dichloro-2-propylmethacrylate, 2-bromoethyl methacrylate, 2-iodoethyl methacrylate, chloromethylmethacrylate, 2-isocyanatoethyl methacrylate, 2-acetoacetoxyethyl methacrylate, phosphorus containing methacrylates such as diethyl[(acryloyloxy)methyl]phosphonate, diethyl[(acryloyloxy)ethyl]phosphonate, diethyl (acryloyloxy)methyl phosphate, and diethyl (acryloyloxy)ethyl phosphate, sulfur-containing methacrylates like 4-thiocyanatobutyl methacrylate, thiocyanathomethyl methacrylate, 2-methylthioethyl methacrylate, 2-methylsulfonyl ethylmethacrylate, 2-ethylthioethylmethacrylate, 2-ethylsulfonyl ethyl methacrylate, 2-propylthioethyl methacrylate, 4-methylthiobutyl methacrylate, 2,3- bis(methylthio)propyl methacrylate, 2,3-bis(methylsulfonyl)propyl methacrylate, 2,3-bis(ethylthio)propyl methacrylate, 2,3-bis(butylsulfonyl)propyl methacrylate, and 2-methylthio-3-ethylthiopropyl methacrylate, silicon-containing methacrylates such as 2-(trimethylsilyloxy)ethylmethacrylate, trimethylsilylmethyl methacrylate, diphenylmethylsilylmethyl methacrylate, ethyl 2-(trimethylsilylmethyl)methacrylate, 3-[tris(trimethylsiloxy)silyl]propylmethacrylate, 3-(trimethoxysilyl)propylmethacrylate, and combinations thereof.

[0062] A more extensive list of exemplary methacrylate monomers, acrylate monomers, methacrylamide monomers, acrylamide monomers, styrenic monomers, diene monomers, vinyl monomers, monomers with reactive functionality, and crosslinking monomers that are suitable for use as the radically polymerizable monomers herein has been described in Moad et al., "Living Radical Polymerization by the RAFT Process - a Third Update," Australian Journal of Chemistry 65: 985-1076 (2012), which is hereby incorporated by reference in its entirety.

Block copolymers

[0063] In a first embodiment, the present invention provides a process for preparing amphiphilic block copolymers comprising blocks [A] and [B],

wherein block [A] is a hydrophilic homo- or copolymer, and

wherein block [B] is a hydrophobic homopolymer having a Tg below 16°C, or a hydrophobic copolymer having a Tg of the hydrophobic block below about 75°C,

wherein the process comprises obtaining blocks [A] and [B] by RDRP, preferably via a RAFT polymerization, of ethylenically unsaturated monomers.

[0064] In this first embodiment, block [A] is a hydrophilic polymer or copolymer that has been formed by the polymerization of one or more monomers as described herein.

[0065] In one example of the first embodiment, block [A] is prepared from one or more of poly(ethylene glycol) methyl ether acrylate (PEGA), poly(ethylene glycol) methyl ether methacrylate (PEGMA), and acrylic acid.

[0066] In this first embodiment, block [B] is a hydrophobic polymer or copolymer that has been formed by the polymerization of one or more monomers as described herein.

[0067] In one example of the first embodiment, block [B] is prepared from one or more of n-butyl acrylate (*n*BA), tert-butyl acrylate (*t*BA), and styrene.

[0068] In a second embodiment, the present invention provides a process for preparing block copolymers comprising blocks [A] and [B],

wherein block [A] is a hydrophobic homo- or copolymer, and

wherein block [B] is a hydrophobic homo- or copolymer,

wherein the process comprises obtaining blocks [A] and [B] by RDRP, preferably via a RAFT polymerization, of ethylenically unsaturated monomers.

[0069] In one example of the second embodiment, block [A] is prepared from poly(methyl methacrylate) (PMMA).

[0070] In one example of the second embodiment, block [B] is prepared from one or more of benzyl methacrylate, ethyl hexyl methacrylate, and methyl methacrylate, preferably PMMA70-b-PBzMA40 or PMMA70-b-P(EHMA90-stat-MMA10).

Glass transition temperature

[0071] As the skilled person will appreciate, the glass transition temperature (Tg) for a polymer is defined as the temperature below which the long-range segmental motion of polymer

chains and the coiling and uncoiling of segments of chains are both "frozen" and the polymer behaves like 'solid glass' or has crystalline properties. Below its Tg, a polymer would not exhibit flow or rubber elasticity, however above its Tg, a polymer exhibits flow or rubber elasticity. In other words, a polymer at a temperature below its Tg is stiffer and less elastic than the same polymer at a temperature above its Tg. The Tg of a polymer may be determined by any standard method known in the art, for example using Differential Scanning Calorimetry (DSC), and Dynamic Mechanical Thermal Analysis (DMTA).

[0072] In embodiments, block [B] comprises a hydrophobic copolymer selected to have a Tg of the hydrophobic block below about 75°C, preferably in the range of -70°C to 75°C.

[0073] In other embodiments, block [B] comprises a hydrophobic homopolymer selected to have a Tg below 16 °C, preferably in the range of -70°C to 16°C.

Reaction conditions

[0074] Conventional techniques, conditions and reagents used in preparing polymer by RAFT polymerization can advantageously be used in accordance with the invention. As a general guide in choosing conditions for polymerization, the concentration of initiator(s), monomers, and other reaction conditions (solvent(s) if any, reaction temperature, reaction pressure, surfactants if any, other additives) should be chosen to optimise polymer properties, *e.g.* narrow dispersity polymers (good control/livingness as per a satisfactory RDRP (RAFT) process).

[0075] Suitable ratios for the monomers of the block [A] (M1:M2), include 1:100 to 100:1, or may be between about 1:100 and 1:1, or between about 1:1 and 1:100, or between about 50:1 and 1:50, or may be about 1:100, 1:95, 1:90, 1:85, 1:80, 1:75, 1:70, 1:65, 1:60, 1:55, 1:50, 1:45, 1:40, 1:35, 1:30, 1:25, 1:20, 1:15, 1:10, 1:9, 1:8, 1:7, 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 15:1, 20:1, 25:1, 30:1, 35:1, 40:1, 45:1, 50:1, 55:1, 60:1, 65:1, 70:1, 75:1, 80:1, 85:1, 90:1, 95:1 or 100:1 or any range therein.

[0076] Suitable ratios for the monomers of the block [B] (M1:M2), include 1:100 to 100:1 or may be between about 1:100 and 1:1, or between about 1:1 and 1:100, or between about 50:1 and 1:50, or may be about 1:100, 1:95, 1:90, 1:85, 1:80, 1:75, 1:70, 1:65, 1:60, 1:55, 1:50, 1:45, 1:40, 1:35, 1:30, 1:25, 1:20, 1:15, 1:10, 1:9, 1:8, 1:7, 1:6, 1:5, 1:4, 1:3, 1:2, 1:1, 2:1, 3:1, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, 15:1, 20:1, 25:1, 30:1, 35:1, 40:1, 45:1, 50:1, 55:1, 60:1, 65:1, 70:1, 75:1, 80:1, 85:1, 90:1, 95:1 or 100:1 or any range therein.

[0077] The chain transfer agent may be present in any suitable concentration, for example between about 1 mmol.L^{-1} and about 1000 mmol.L^{-1}, or between about 10 mmol.L^{-1} and about 1000 mmol.L^{-1}, such as between about 5 mmol.L^{-1} and 20 mmol.L^{-1}, or between about 7 mmol.L^{-1} and about 13 mmol.L^{-1}, or about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 mmol.L^{-1} or any range therein.

[0078] In an embodiment, the ratio of [hydrophobic monomer]:[chain transfer agent] is in the range of about 10 to about 400, or between about 100 to about 150, or between about 75 and about 100, or it may be about 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195 or 200 or any range therein. In one preferred embodiment, the ratio is in the range of about 40 to about 200.

[0079] The polymerization temperature will be optimisable by the skilled person, taking into consideration the specific monomer(s) being polymerized and other components of the polymerization or reaction medium.

[0080] Polymerization will generally be conducted at temperatures in the range of 20 to 100 °C, such as between about 0 and 180 °C, or between about 50 and 150 °C, or at about 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100°C or any range therein, preferably in the range of 40 to 100°C.

[0081] Reaction times can range from 1 to 48 hours, for instance, from 1 to 20 hours, from 1 to 12 hours, or from 1 to 8 hours, or about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23 or 24 hours or any range therein.

[0082] The polymerization may be conducted at any suitable pH range. In one embodiment, the pH is in the range of 3 to 8, or it may be between about 3.5 and about 6, or between about 4 and about 7, or at about 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5 or 8 or any range therein.

[0083] In an embodiment, polymerization was carried out at 80°C in an oil bath with a stirring speed of 350 rpm for 6 hours.

[0084] The reaction medium can be chosen from a wide range of media to suit the monomer(s) being used. For example, water and alcohols, such as methanol, ethanol, n-propanol, isopropylalcohol, n-butanol, n-pentanol, and mixtures thereof.

[0085] The reaction medium can further include one or more of an acid, a base, a catalyst, a surfactant, and/or a coupling agent or any other suitable component.

Hydrophobic and hydrophilic

[0086] Those skilled in the art will appreciate that the terms "hydrophilic" and "hydrophobic" used herein are not intended to define absolute qualities of a particular substance but rather to be an indicator of a favourable or unfavourable interactions (i.e., attractive or repulsive interactions). In other words, the terms "hydrophilic" and "hydrophobic" are used herein as primary indicators to define characteristics such as like attracting like and unlike repelling unlike.

[0087] As a convenient point of reference only, a person skilled in the art might consider a "hydrophilic" liquid to have a solubility in water of at least 5 g/L at 25°C, and a "hydrophobic" liquid to have a solubility in water of less than 5 g/L at 25°C. In terms of a solid, the terms "hydrophilic" and "hydrophobic" might be considered by a person skilled in the art to be a reference to a solid which could be wetted by (i.e., does not repel) a hydrophilic and hydrophobic liquid, respectively.

Molecular weights and dispersity index

[0088] Those skilled in the art will appreciate that polymers exist as a distribution of chain lengths and molecular weights. Therefore, the molecular weight of a polymer must be described as an average molecular weight calculated from the molecular weights of all the chains in the sample.

[0089] In the present invention, the molecular weight (MW) of block [A] or block [B] may be in the range of 5000 to 100,000, of it may be between about 10,000 and 100,000, or between about 25,000 and about 75,000, or it may be about 5000, 5500, 6000, 6500, 7000, 7500, 8000, 8500, 9000, 9500, 10000, 11000, 12000, 13000, 14000, 15000, 16000, 17000, 18000, 19000, 20000, 25000, 30000, 35000, 40000, 45000, 50000, 60000, 70000, 80000, 90000, 100000, 125000, 150000, 175000, 200000, 225000, 250000, 275000, 300000, 350000, 400000, 450000 or 500000 or any range therein. In a preferred embodiment, the molecular weight of block [A] or block [B] is in the range of 5000-40,000.

[0090] In the present invention, the average degree of polymerization (DP) of a block copolymer as described herein is a value ranging from about 10 to about 1000, or between about 20 and about 500, or between about 50 and 750, or between and 300 and about 800, or about 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195 or 200 or any range therein. In a preferred embodiment, the degree of polymerization (DP) of the block copolymer is in the range

of about 50 to about 300.

[0091] Polymers prepared by the present invention can advantageously exhibit a well-defined molecular architecture, a predetermined molecular, weight and a narrow molecular weight distribution or low dispersity (*Đ*).

Nanofiber dimensions

[0092] As the skilled person would appreciate, the nanofibers of the present invention are defined as having a length that exceeds, or greatly exceeds, the width of the nanofibers. The ratio of length to width of the nanofibers may be greater than 5:1, or greater than 10:1, or greater than 25:1, or greater than 50:1, or greater than 100:1, or greater than 250:1, or greater than 500:1, or greater than 1000:1, or it may be between 5:1 and 200,000:1, or between 100:1 and 10,000:1, or between 500:1 and 5,000:1, or any range therein.

[0093] The width of the nanofibers may be between about 1 nm and about 250 nm, or between about 3 nm and about 100 nm, or between 5 nm and about 50 nm, or about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160 ,165, 170, 175, 180, 185, 190, 195, 200, 205, 210, 215, 220, 225, 230, 235, 240, 245 or 250 nm or any range therein.

[0094] The length of each of the nanofibers may be between about 5 nm and 2 mm, or between about 10 nm and about 1 mm, or between about 50 nm and about 500 μm, or between about 20 nm and about 100 μm, or about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900 or 1000 nm, or 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900 or 1000 μm, or about 1.5 or 2 mm or any range therein.

Crosslinkers

[0095] In certain embodiments, the amphiphilic block copolymer may be crosslinked to permanently stabilise the obtained nanofibers, and hence to give them long term stability. The crosslinker may provide a covalently-bound bridge between two different polymer chains. Any suitable crosslinking agent may be used. As the skilled person would appreciate, the crosslinker must have two terminal groups that are capable of radical polymerization and therefore

incorporation into the polymer chain of the present invention. Examples of suitable crosslinking agents include, but are not limited to, an ethylene glycol diacrylate ester (e.g., ethylene glycol dimethylacrylate) when the monomeric material is an acrylate ester or an ethylene glycol diacrylic acid (e.g. ethylene glycol dimethacrylic acid) when the monomeric material is an acrylic acid. In embodiments where a crosslinking agent is present, the molar ratio of monomeric material to crosslinking agent in the solvent may be from 10:1 to 50:1, such as from 20:1 to 40:1.

[0096] Non limiting examples of crosslinkers include (meth)acrylic anhydride, divinyl ethers of compounds selected from the group consisting of ethylene glycol, ethylene glycol diacrylate, poly(ethylene glycol) diacrylate, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,11-unidecanediol, 1,12-dodecanediol, and combinations thereof; divinyl ethers of diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, hexaethylene glycol, heptaethylene glycol, octaethylene glycol, nonaethylene glycol, decaethylene glycol, and polyalkylene glycols; methylenebis(meth)acrylamide; ethylene glycol di(meth)acrylate; butanediol di(meth)acrylate; tetraethylene glycol di(meth)acrylate; polyethylene glycol di(meth)acrylate; polyethylene glycol di(meth)acrylamide; dipropylene glycol diallyl ether; polyglycol diallyl ether; hydroquinone diallyl ether; trimethylolpropane tri(meth)acrylate; trimethylolpropane diallyl ether; pentaerythritol triallyl ether; allyl(meth)acrylate; triallyl cyanurate; diallyl maleate; polyallyl esters; tetraallyloxyethane; triallylamine; tetraallylethylenediamine; divinyl benzene; glycidyl(meth)acrylate; 1,7-octadiene; 1, 9-decadiene; 1, 13-tetradecadiene; divinylbenzene; diallyl phthalate; triallyl-l,3,5-triazine-2,4,6(1H,3H,5H)-trione; N,N'-divinylimidazolidone; l-vinyl-3(E)-ethylidene pyrrolidone; 2,4,6-triallyloxy-1,3,5-triazine; and combinations thereof.

[0097] In one non-limiting embodiment, the crosslinker is selected from the group consisting of (meth)acrylic anhydride, methylenebis(meth)acrylamide, ethylene glycol di(meth)acrylate, butanediol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylamide, dipropylene glycol diallyl ether, polyglycol diallyl ether, hydroquinone diallyl ether, trimethylolpropane tri(meth)acrylate, trimethylolpropane diallyl ether, pentaerythritol triallyl ether, and combinations thereof.

[0098] In the present invention, the crosslinker may be added at any time-point of polymerization of the second block, including at the beginning, middle, or end. In an embodiment, the crosslinker is added at t=0 h. In other embodiments, the crosslinker is added at t=2 h. It is envisioned that the skilled person will be able to optimise the timing of the addition of

the crosslinker, depending on the effect sought; for instance, adding the crosslinker later in the polymerization process may result in a lesser influence exerted by the crosslinker over the final morphology, and *vice versa*.

[0099] In one non-limiting embodiment, the crosslinker(s) can be present in an amount from about 0.001 % by weight to about 20 % by weight of the block copolymer. In another nonlimiting embodiment, the crosslinker(s) can be present in an amount from about 0.001 % by weight to about 10 % by weight of the block copolymer. In yet another non-limiting embodiment, the crosslinker(s) can be present in an amount from about 0.001 % by weight to about 5 % by weight of the block copolymer. The cross-linker may be present at about 0.001, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 % by weight or any range therein.

[00100] In one embodiment, the crosslinker is ethylene glycol diacrylate (EGDA) or ethylene glycol dimethacrylate (EGDMA).

[00101] In another embodiment, the crosslinker is poly(ethylene glycol) diacrylate (PEGDA).

Uses of the nanofibers of the invention

[00102] The nanofibers disclosed herein may be used as a vehicle for an active agent. In other words, said nanofibers may further comprise an active agent encapsulated in the nanofibers. When used herein, the term "encapsulated" refers to the enclosure of an active agent within the core of body of the nanofibers described herein. For example, in embodiments of the invention where the nanofibers have a solid core then the active agent will be held within the polymer matrix of the nanofibers in the core of said nanofibers.

[00103] In embodiments of the invention, nanofiber compositions that further comprise an active agent may contain from 0.01 to 50 weight% of the active agent relative to the weight of the nanofibers as a whole. For example, the active agent may be present in an amount of from 1 to 30 weight%, such as from 5 to 10 weight% relative to the weight of the nanofibers as a whole. The active agent may be selected from one or more of the group consisting of vitamin C, peptides, glycerol, dyes, flavours, perfume oils, citronellal, silicon oils, organosilicons, pesticides, beta-carotene and a pharmacologically active agent.

[00104] The term "pharmacologically active agent" when used herein may refer to a substance useful for the treatment of or the prevention of a condition affecting a human or other animal. Said condition may be a disease, a disorder or a physiological condition. It will be

appreciated that the active agent may not directly affect the underlying condition, but may be used as an adjuvant with a further active agent to enhance the effectiveness of the other active agent. Thus, the term "pharmacologically active agent" herein incudes all classes of pharmacologically active agents, whether adjuvant or therapeutic, that may be provided to a subject through oral administration. When used herein, the term "pharmacologically active agent" and "drug" may be used interchangeably and so the term "drug" may be interpreted based on the definition of "active agent". Examples of pharmacologically active agents include, but are not limited to ibuprofen, fenofibrate, and isotrentinoin.

[00105] Further active agents that may be mentioned herein may include, but are not limited to, carbon metabolites (e.g. glucose, fructose, fumarate, etc.), electron acceptors (e.g. nitrate, peroxide, etc.), as well as a vitamin, such as vitamin A, B1, B2, B3, B6, B12, D, E, biotin, folate, and panothenate; minerals such as calcium, magnesium, selenium, and zinc; an amino acid such as asparagine, carnitine, glutamine, and serine; an antioxidant selected from coenzyme Q10, glutathione, and cysteine; or a metabolite such as lipoic acid, oleic add, choline, inositol, fructose, glucose, insulin, epigallocatechin gallate, and mixtures thereof.

[00106] In embodiments of the invention, the nanofibers may have a core region that may comprise an active agent. The nature of the active agent in the core will be determined by the nature of the nanofibers that have been formed. For example, nanofibers formed such that the hydrophilic blocks of the amphiphilic block copolymer are arranged on the surface of the nanofibers may be suitable for the encapsulation of hydrophobic active agents (as described hereinbefore). Alternatively, nanofibers are formed such that the hydrophobic blocks of the amphiphilic block copolymer are arranged on the surface of the nanofibers may be suitable for the encapsulation of hydrophilic active agents (as described hereinbefore). The nanofibers of the invention may have an average diameter of from 50 to 200 nm, such as from 70 to 150 nm.

[00107] In some materials, the hydrophobic repeating units will form the surface of the nanofibers, with the hydrophilic repeating units forming the core. In other embodiments that have the opposite arrangement, the hydrophilic repeating units will form the surface of the nanofibers, with the hydrophobic repeating units forming the core. In yet further embodiments, the hydrophobic repeating units will form the surface of the nanofibers, with hydrophobic repeating units also forming the core.

[00108] Other uses of the nanofibers of the invention relate to: sun care compositions, face care compositions, lip care compositions, eye care compositions, skin care compositions, after-sun compositions, body care compositions, nail care compositions, anti-aging compositions,

insect repellants, oral care compositions, deodorant compositions, hair care compositions, conditioning compositions, color cosmetic compositions, color-protection compositions, self-tanning compositions, and foot care compositions.

[00109] The nanofibers disclosed herein may also be used as a filler and/or a reinforcing agent for a composite material. In other words, said nanofibers may be encapsulated in, or dispersed through, a matrix material. The nanofibers may alter the physical properties of the formed composite material. The nanofibers may be added to, or dispersed throughout, the matrix during production of the composite material, such as when the matrix is dissolved in or dispersed throughout a solvent such as water, or is molten. In one example, the matrix may comprise a polymer as described herein so as to form a composite polymer material, such as a film, or a coating, or a formed article. The polymer matrix may preferably be hydrophilic, or formed from an aqueous dispersion, so that the hydrophilic shell of the nanofibers is wetted by the matrix during production. When the polymer matrix is formed from an aqueous dispersion (i.e., latex), the nanofibers may be mixed with the aqueous dispersion before curing. When the polymer matrix is molten, the nanofibers may be added to an extruder with the polymer pellets and mixed during or after the melting of the polymer matrix material.

[00110] In another example, the matrix may comprise a hydraulic binder, such as cement (e.g., Portland cement) or fly ash, in which the nanofibers may be added to hydraulic binder before addition of water, or after the addition of water, or sequentially with the water, and then mixed to produce a cementitious material comprising the nanofibers of the present invention.

[00111] In another example, the matrix may comprise a mineral material, such as calcium sulfate (i.e., gypsum) in the production of plaster-based articles, such as plasterboard/drywall.

[00112] In yet another example, the matrix may be any substance that would benefit from modification of the viscosity and/or rheology of the matrix. In other words, the nanofibers may be used as viscosity modifiers for a range of liquid or semi-solid materials, such as gels, hydraulic fluids and the like.

[00113] As the skilled person would appreciate, the nanofibers of the present invention may be used to replace fillers and/or reinforcing agents in other known materials, in which the effect of the low Tg core would result in a beneficial effect.

BRIEF DESCRIPTION OF DRAWINGS

[00114] Preferred features, embodiments and variations of the invention may be discerned

from the following Detailed Description which provides sufficient information for those skilled in the art to perform the invention. The Detailed Description is not to be regarded as limiting the scope of the preceding Summary of the Invention in any way. The Detailed Description will make reference to a number of drawings as follows:

[00115] **Figure 1.** Overall monomer conversion for RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent at pH 3.5, pH 5, and pH 7 (see also Table 1).

[00116] **Figure 2.** Molecular weight distributions (w(log M) vs. log M) of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent at pH 3.5, pH 5, and pH 7 (see also Table 1).

[00117] **Figure 3.** TEM images of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent performed at pH 3.5, pH 5, and pH 7. ([styrene]/[*n*BA] = 70/30, [hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 200) (see also Table 1). Scale bars: A-1 = 500 nm, A-2 = 2 μm, A-3 = 500 nm.

[00118] **Figure 4.** Molecular weight distributions (w(log M) vs. log M) of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent with different [hydrophobic monomer]$_0$/[macroRAFT]$_0$ (macroRAFT agent, [hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 50 (B-1), 100 (B-2), 130 (B-3), 150 (B-4), 170 (B-5), 200 (B-6) from left to right) (see also Table 2).

[00119] **Figure 5.** TEM images of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent performed at pH 5 with different [hydrophobic monomer]$_0$/[macroRAFT]$_0$ ([hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 50 (B-1), 100 (B-2), 130 (B-3), 150 (B-4), 170 (B-5), 200 (B-6) (see also Table 2). Scale bar: B-1 = 200 nm, B-2 = 1 μm, B-3 = 1 μm, B-4 = 2 μm, B-5 = 2 μm, B-6 = 2 μm.

[00120] **Figure 6.** TEM images of nanoparticles synthesized via RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent at pH 5 with EGDA or PEGDA at t = 0 h, Method (i) (*Entries* C-x and D-x; top frame) and at t = 2 h, Method (ii) (*Entries* E-x and F-x; bottom frame) ([hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 100). Scale bars: B-2 = 1 μm, C-1 = 1 μm, C-2 = 1 μm, D-1 = 1 μm, D-2 = 1 μm, D-3 = 100 nm, E-1 = 1 μm, E-2 = 1 μm, F-1 = 1 μm, F-2 = 1 μm, F-3 = 500 nm.

[00121] **Figure 7.** EGDA or PEGDA crosslinked P(AA-*stat*-PEGA)-*b*-P(S-*stat*-*n*BA) nanoparticles dissolved in THF (a) no crosslinker added, 1 mol% PEGDA added at $t = 0$ h, 2.5 mol% PEGDA added at $t = 0$ h (from top left to right) (b) no crosslinker added, 0.5 mol% EGDA added at $t = 0$ h, 1 mol% EGDA added at $t = 0$ h, 10 mol% EGDA added at $t = 0$ h (from top left to right) (c) no crosslinker added, 1 mol% PEGDA added at $t = 2$ h, 10 mol% PEGDA at $t = 2$ h (from bottom left to right) (d) no crosslinker added, 3 mol% EGDA added at $t = 2$ h, 5 mol% EGDA added at $t = 2$ h, 10 mol% EGDA added at $t = 2$ h (from bottom left to right).

[00122] **Figure 8.** TEM images of nanoparticles synthesized via RAFT aqueous emulsion polymerization of styrene and *n*BA ($[\text{styrene}]_0/[n\text{BA}]_0 = 20/80$) in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent at pH 5 with 5 mol% EGDA (relative to macroRAFT agent) after 2 h of polymerization with different solids content ($[\text{hydrophobic monomer}]_0/[\text{macroRAFT}]_0 = 130$, solids content 15.2% (H-1), 24.7% (H-2), 32.7% (H-3)). Scale bars: H-1 = 200 nm, H-2 = 200 nm, H-3 = 200 nm.

[00123] **Figure 9.** Molecular weight distributions (w(log M) vs. log M) of P(AA-*stat*-PEGA)-TTC macroRAFT agent (M_n = 13,400 g/mol; $Đ = 1.20$).

[00124] **Figure 10.** TEM images of nanoparticles synthesized via RAFT aqueous emulsion polymerization of styrene and *n*BA ($[\text{styrene}]_0/[n\text{BA}]_0 = 20/80$) in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent at pH 5 with 5 mol% EGDA (relative to macroRAFT agent) after 2 h of the polymerization with different $[\text{hydrophobic monomer}]_0/[\text{macroRAFT}]_0$ ($[\text{hydrophobic monomer}]_0/[\text{macroRAFT}]_0 = 80$ (G-1), 100 (G-2), 115 (G-3), 130 (G-4), 150 (G-5), 180 (G-6), 200 (G-7), 250 (G-8), 300 (G-9)). Scale bars: G-1 = 200 nm, G-2 = 1 µm, G-3 = 100 nm, G-4 = 1 µm, G-5 = 1 µm, G-6 = 1 µm, G-7 = 2 µm, G-8 = 1 µm, G-9 = 2 µm.

[00125] **Figure 11.** Schematic illustration of block copolymers with a first hydrophilic block and a second hydrophobic block self-assembled into nanofibers with a hydrophilic outside 'shell' portion and a hydrophobic inside 'core' portion used in the preparation of nanofiber-reinforced nanocomposite polymer materials.

[00126] **Figure 12.** (A) TEM micrograph of PMMA-*b*-P(EHMA-*stat*-MMA) and (B) SEM micrograph of PMMA-*b*-PBzMA.

DEFINITIONS

[00127] In describing and claiming the present invention, the following terminology will be used in accordance with the definitions set out below. It is also to be understood that the

terminology used herein is for the purpose of describing particular embodiments of the invention only and is not intended to be limiting.

[00128] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one having ordinary skill in the art to which the invention pertains.

[00129] Unless the context clearly requires otherwise, throughout the description and the claims, the terms “comprise”, “'comprising”, and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”. For example, a composition, mixture, process or method that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, mixture, process or method.

[00130] The transitional phrase "consisting of” excludes any element, step, or ingredient not specified. If in the claim, such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consisting of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

[00131] The transitional phrase "consisting essentially of" is used to define a composition, process or method that includes materials, steps, features, components, or elements, in addition to those literally disclosed, provided that these additional materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention. The term "consisting essentially of" occupies a middle ground between "comprising" and "consisting of".

[00132] Where applicants have defined an invention or a portion thereof with an open-ended term such as "comprising", it should be readily understood that (unless otherwise stated) the description should be interpreted to also describe such an invention using the terms "consisting essentially of" or "consisting of." In other words, with respect to the terms “comprising”, “consisting of”, and “consisting essentially of”, where one of these three terms is used herein, the presently disclosed and claimed subject matter may include the use of either of the other two terms. Thus, in some embodiments not otherwise explicitly recited, any instance of “comprising” may be replaced by “consisting of” or, alternatively, by “consisting essentially of”.

[00133] Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not

to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[00134] Also, the indefinite articles "a" and "an" preceding an element or component of the invention are intended to be non-restrictive regarding the number of instances (i.e., occurrences) of the element or component. Therefore "a" or "an" should be read to include one or at least one, and the singular word form of the element or component also includes the plural unless the number is obviously meant to be singular.

[00135] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term “about”. The examples are not intended to limit the scope of the invention. In what follows, or where otherwise indicated, “%” will mean “weight %”, “ratio” will mean “weight ratio” and “parts” will mean “weight parts”.

[00136] The terms “predominantly” and “substantially” as used herein shall mean comprising more than 50% by weight, unless otherwise indicated.

[00137] As used herein, with reference to numbers in a range of numerals, the terms "about," "approximately" and "substantially" are understood to refer to the range of -10% to +10% of the referenced number, preferably -5% to +5% of the referenced number, more preferably -1 % to + 1 % of the referenced number, most preferably -0 .1 % to +0 .1 % of the referenced number. Moreover, with reference to numerical ranges, these terms should be construed as providing support for a claim directed to any number or subset of numbers in that range. For example, a disclosure of from 1 to 10 should be construed as supporting a range of from 1 to 8, from 3 to 7, from 1 to 9, from 3.6 to 4.6, from 3.5 to 9.9, from 8 to 10, and so forth.

[00138] As used herein, wt.% refers to the weight of a particular component relative to total weight of the referenced composition.

[00139] The term "and/or" used in the context of "X and/or Y" should be interpreted as "X," or "Y," or "X and Y." Similarly, "at least one of X or Y" should be interpreted as "X," or "Y," or "both X and Y."

[00140] The terms “preferred” and “preferably” refer to embodiments of the invention that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more

preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the invention.

[00141] The complete disclosures of the patents, patent documents and publications cited herein are incorporated by reference in their entirety as if each were individually incorporated.

[00142] As used herein, the term "nanofiber" refers to a solid nanoparticulate material that is similar to a micelle in that it has a solid core and a solid shell/corona (i.e., the interior portion of the cylinder is not hollow). In other words, the core and shell are formed from the polymeric material, with the hydrophilic blocks on the exterior surface of the nanofiber (to form the shell) and the hydrophobic blocks forming the core of the nanofiber (or vice versa). In another embodiment, the hydrophobic blocks are on the exterior surface of the nanofiber with hydrophobic blocks also forming the core of the nanofiber. While the shell is solid, these nanofiber may have the capacity to be used as a carrier because other molecules (e.g., active agents) can still be dispersed within the core of the cylindrical nanofiber (e.g. by diffusion or other suitable means), thereby allowing the cylindrical nanofiber to act as a carrier for an active agent.

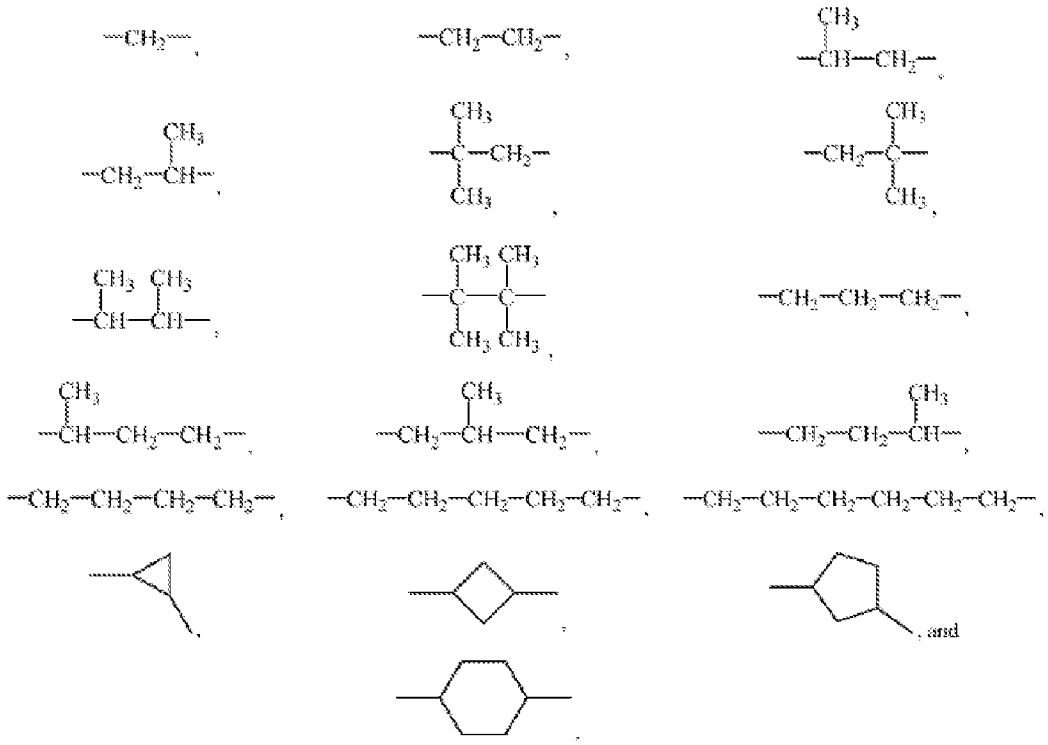
[00143] The term "each independently selected from the group consisting of" means when a group appears more than once in a structure, that group can be selected independently each time it appears.

[00144] The term "alkyl" refers to a functionalized or unfunctionalized, monovalent, straight chain, branched-chain, or cyclic C_1-C_{60} hydrocarbyl group optionally having one or more heteroatoms. In one non-limiting embodiment, an alkyl is a C_1-C_{45} hydrocarbyl group. In another non-limiting embodiment, an alkyl is a C_1-C_{30} hydrocarbyl group. Non-limiting examples of alkyl include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, tert-octyl, iso-norbomyl, n-dodecyl, tert-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, n-eicosyl, cyclobutyl, cyclopentyl, cyclohexyl, and the like. The definition of "alkyl" also includes groups obtained by combinations of straight-chain, branched-chain and/or cyclic structures.

[00145] The term "aryl" refers to a functionalized or unfunctionalized, monovalent, aromatic hydrocarbyl group optionally having one or more heteroatoms. The definition of aryl includes carbocyclic and heterocyclic aromatic groups. Non-limiting examples of aryl groups include phenyl, naphthyl, indenyl, indanyl, azulenyl, fluorenyl, anthracenyl, furyl, thienyl, pyridyl, pyrrolyl, oxazolyl, thiazolyl, imidazolyl, pyrazolyl, 2-pyrazolinyl, pyrazolidinyl, isoxazolyl,

isothiazolyl, 1,2,3-oxadiazolyl, 1,2,3-triazolyl, 1,3,4-thiadiazolyl, pyridazinyl, pyrimidinyl, pyrazinyl, 1,3,5-triazinyl, 1,3,5-trithianyl, indolizinyl, indolyl, isoindolyl, 3H-indolyl, indoliny1, benzo[b]furany1, 2,3-dihydrobenzofurany1, benzo[b]thiophenyl, 1H-indazolyl, enzimidazolyl, benzthiazolyl, purinyl, 4H-quinolizinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, 1,8-naphthridinyl, pteridinyl, carbazolyl, acridinyl, phenazinyl, phenothiazinyl, phenoxyazinyl, pyrazolo[l,5-c]triazinyl, and the like.

[00146] The term "alkylene" refers to a functionalized or unfunctionalized, divalent, straight chain, branched-chain, or cyclic C_1-C_{40} hydrocarbyl group optionally having one or more heteroatoms. In one non-limiting embodiment, an alkylene is a C_1-C_{30} group. In another nonlimiting embodiment, an alkylene is a C_1-C_{20} group. Non-limiting examples of alkylene groups include:



[00147] The term "heteroatom" refers to oxygen, nitrogen, sulfur, silicon, phosphorous, or halogen. The heteroatom(s) can be present as a part of one or more heteroatom-containing functional groups. Non-limiting examples of heteroatom-containing functional groups include ether, hydroxy, epoxy, carbonyl, carboxamide, carboxylic ester, carboxylic acid, imine, imide, amine, sulfonic, sulfonamide, phosphonic, and silane groups. The heteroatom(s) can also be present as a part of a ring such as in heteroaryl and heteroarylene groups.

[00148] The term “alkenyl” as used herein denotes groups formed from straight chain,

branched or cyclic hydrocarbon residues containing at least one carbon to carbon double bond including ethylenically mono-, di- or polyunsaturated alkyl or cycloalkyl groups as previously defined, preferably C_{2-20} alkenyl (e.g. C_{2-10} or C_{2-6}). Examples of alkenyl include vinyl, allyl, 1-methylvinyl, butenyl, iso-butenyl, 3-methyl-2-butenyl, 1-pentenyl, cyclopentenyl, 1-methyl-cyclopentenyl, 1-hexenyl, 3-hexenyl, cyclohexenyl, 1-heptenyl, 3-heptenyl, 1-octenyl, cyclooctenyl, 1-nonenyl, 2-nonenyl, 3-nonenyl, 1-decenyl, 3-decenyl, 1,3-butadienyl, 1,4-pentadienyl, 1,3-cyclopentadienyl, 1,3-hexadienyl, 1,4-hexadienyl, 1,3-cyclohexadienyl, 1,4-cyclohexadienyl, 1,3-cycloheptadienyl, 1,3,5- cycloheptatrienyl and 1,3,5,7-cyclooctatetraenyl. An alkenyl group may be optionally substituted by one or more optional substituents as herein defined.

[00149] The term "alkynyl" as used herein denotes groups from straight chain, branched or cyclic hydrocarbon residues containing at least one carbon-carbon triple bond including ethylenically mono-, di- or polyunsaturated alkyl or cycloalkyl groups as previously defined. Unless the number of carbon atoms is specified the term preferably refers to C_{2-20} alkynyl (e.g. C_{2-10} or C_{2-6}), Examples include ethynyl, 1-propynyl, 2-propynyl, and butynyl isomers, and pentynyl isomers. An alkynyl group may be optionally substituted by one or more optional substituents as herein defined.

[00150] The term "carbocyclyl" refers to non-aromatic monocyclic, polycyclic, fused or conjugated hydrocarbon residues, preferably C_{3-20} (e.g. C_{3-10} or C_{3-8}). The rings may be saturated, e.g. cycloalkyl, or may possess one or more double bonds (cycloalkenyl) and/or one or more triple bonds (cycloalkynyl). Particularly preferred carbocyclyl moieties are 5-6 membered or 9-10 membered ring systems. Suitable examples include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclopentenyl, cyclohexenyl, cyclooctenyl, cyclopentadienyl, cyclohexadienyl, cyclooctatetraenyl, indanyl, decalinyl and indenyl. A carbocyclyl group may be optionally substituted by one or more optional substituents as herein defined. The term "carbocyclylene" is intended to denote the divalent form of carbocyclyl.

[00151] The term "heterocyclyl" refers to a stable 3- to 18-membered ring (radical) which consists of carbon atoms and from one to five heteroatoms selected from the group consisting of nitrogen, oxygen, and sulfur. Thes heterocycle may be a monocyclic, or a polycyclic ring system, which may include fused, bridged, or spiro ring systems; and the nitrogen, carbon, or sulfur atoms in the heterocycle may be optionally oxidized; the nitrogen atom may be optionally quaternized; and the ring may be partially or fully saturated. Examples of such heterocycles

include, without limitation, azepinyl, azocanyl, pyranyl, dioxanyl, dithianyl, 1,3-dioxolanyl, tetrahydrofuryl, dihydropyrrolidinyl, decahydroisoquinolyl, imidazolidinyl, isothiazolidinyl, isoxazolidinyl, morpholinyl, octahydroindolyl, octahydroisoindolyl, 2-oxopiperazinyl, 2-oxopiperidinyl, 2-oxopyrrolidinyl, 2-oxoazepinyl, oxazolidinyl, oxiranyl, piperidinyl, piperazinyl, 4-piperidonyl, pyrrolidinyl, pyrazolidinyl, thiazolidinyl, tetrahydropyranyl, thiamorpholinyl, thiamorpholinyl sulfoxide, and thiamorpholinyl sulfone.

[00152] The term "heteroaryl" means an aromatic monocyclic or multi-cyclic ring system of about 5 to about 19 ring atoms, or about 5 to about 10 ring atoms, in which one or more of the atoms in the ring system is/are element(s) other than carbon, for example, nitrogen, oxygen, or sulfur. In the case of multi-cyclic ring system, only one of the rings needs to be aromatic for the ring system to be defined as "heteroaryl". Particular heteroaryls contain about 5 to 6 ring atoms. The prefix aza, oxa, thia, or thio before heteroaryl means that at least a nitrogen, oxygen, or sulfur atom, respectively, is present as a ring atom. A nitrogen, carbon, or sulfur atom in the heteroaryl ring may be optionally oxidized; the nitrogen may optionally be quaternized. Representative heteroaryls include pyridyl, 2-oxo-pyridinyl, pyrimidinyl, pyridazinyl, pyrazinyl, triazinyl, furanyl, pyrrolyl, thiophenyl, pyrazolyl, imidazolyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, triazolyl, oxadiazolyl, thiadiazolyl, tetrazolyl, indolyl, isoindolyl, benzofuranyl, benzothiophenyl, indolinyl, 2-oxoindolinyl, dihydrobenzofuranyl, dihydrobenzothiophenyl, indazolyl, benzimidazolyl, benzooxazolyl, benzothiazolyl, benzoisoxazolyl, benzoisothiazolyl, benzotriazolyl, benzo[1,3]dioxolyl, quinolinyl, isoquinolinyl, quinazolinyl, cinnolinyl, pthalazinyl, quinoxalinyl, and the like.

[00153] The term “acyl” denotes a group containing the moiety C=O such as C(O)-R^e, including wherein the "acyl" group is in turn attached through an oxygen atom -C(O)O-R^e, such as carboxylic acid, esters, amides. Preferred acyl groups include wherein R^e is hydrogen or an alkyl, alkenyl, alkynyl, aryl, heteroaryl, carbocyclyl, or heterocyclyl residue. Examples of acyl include formyl, straight chain or branched alkanoyl (e.g. C_{1-20}) such as acetyl, propanoyl, butanoyl, 2-methylpropanoyl, pentanoyl, 2,2-dimethylpropanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, nonadecanoyl and icosanoyl; cycloalkylcarbonyl such as cyclopropylcarbonyl, cyclobutylcarbonyl, cyclopentylcarbonyl and cyclohexylcarbonyl; aroyl such as benzoyl, toluoyl and naphthoyl; aralkanoyl such as phenylalkanoyl (e.g. phenylacetyl, phenylpropanoyl, phenylbutanoyl, phenylisobutylyl, phenylpentanoyl and phenylhexanoyl) and naphthylalkanoyl (e.g. naphthylacetyl, naphthylpropanoyl and naphthylbutanoyl]; aralkenoyl such as phenylalkenoyl (e.g. phenylpropenoyl, phenylbutenoyl,

phenylmethacryloyl, phenylpentenoyl and phenylhexenoyl and naphthylalkenoyl (e.g. naphthylpropenoyl, naphthylbutenoyl and naphthylpentenoyl); aryloxyalkanoyl such as phenoxyacetyl and phenoxypropionyl; arylthiocarbamoyl such as phenylthiocarbamoyl; arylglyoxyloyl such as phenylglyoxyloyl and naphthylglyoxyloyl; arylsulfonyl such as phenylsulfonyl and napthylsulfonyl; heterocycliccarbonyl; heterocyclicalkanoyl such as thienylacetyl, thienylpropanoyl, thienylbutanoyl, thienylpentanoyl, thienylhexanoyl, thiazolylacetyl, thiadiazolylacetyl and tetrazolylacetyl; heterocyclicalkenoyl such as heterocyclicpropenoyl, heterocyclicbutenoyl, heterocyclicpentenoyl and heterocyclichexenoyl; and heterocyclicglyoxyloyl such as thiazolyglyoxyloyl and thienylglyoxyloyl. The R^e residue may be optionally substituted as described herein.

[00154] The term "sulfoxide" refers to a group -S(O)R_f wherein R_f is selected from hydrogen, alkyl, alkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, carbocyclyl, and aralkyl. Examples of preferred R include C_{1-20}alkyl, phenyl and benzyl.

[00155] The term "sulfonyl" refers to a group $S(O)_2$-R_f, wherein R_f is selected from hydrogen, alkyl, alkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, carbocyclyl and aralkyl. Examples of preferred R_f include C_{1-20}alkyl, phenyl, and benzyl.

[00156] The term "sulfonamide" refers to a group S(O)N$R_f$$R_f$ wherein each R_f is independently selected from hydrogen, alkyl, alkenyl, alkynyl, aryl, heteroaryl, heterocyclyl, carbocyclyl, and aralkyl. Examples of preferred R_f include C_{1-20}alkyl, phenyl and benzyl. In one embodiment at least one R_f is hydrogen. In another embodiment, both R_f are hydrogen.

[00157] The term "amino" is used here in its broadest sense as understood in the art and includes groups of the formula NR^aR^b wherein R^a and R^b may be independently selected from hydrogen, alkyl, alkenyl, alkynyl, aryl, carbocyclyl, heteroaryl, heterocyclyl, arylalkyl, and acyl. R^a and R^b together with the nitrogen to which they are attached, may also form a monocyclic, or polycyclic ring system e.g. a 3-10 membered ring, particularly, 5-6 and 9-membered systems. Examples of "amino" include NH_2, NHalkyl (e.g. C_{1-20}alkyl), NHaryl (e.g. NHphenyl), NHaralkyl (e.g. NHbenzyl), NHacyl (e.g. NHC(O)C_{1-20} alkyl, NHC(O)phenyl), Nalkylalkyl (wherein each alkyl, for example C_{1-20}, may be the same or different) and 5 or 6 membered rings, optionally containing one or more same or different heteroatoms (e.g. O, N and S).

[00158] The term "amido" is used here in its broadest sense as understood in the art and includes groups having the formula $C(O)NR^aR^b$, wherein R^a and R^b are as defined as above. Examples of amido include $C(O)NH_2$, C(O)NHalkyl (e.g. C_{1-20}alkyl), C(O)NHaryl (e.g.

C(O)NHphenyl), C(O)NHaralkyl (e.g. C(O)NHbenzyl), C(O)NHacyl (e.g. C(O)NHC(O)C_{1-20}alkyl, C(O)NHC(O)phenyl), C(O)Nalkylalkyl (wherein each alkyl, for example C_{1-20}, may be the same or different) and 5 or 6 membered rings, optionally containing one or more same or different heteroatoms (e.g. O, N and S).The term "halogen" or "halo" refers to Cl, Br, I, or F.

[00159] The terms written as "[groupA][group B]" refer to group A when linked by a divalent form of group B. For example, "[group A][alkyl]" refers to a particular group A (such as hydroxy, amino, etc.) when linked by divalent alkyl, i.e. alkylene (e.g. hydroxyethyl is intended to denote HO-CH2-CH-). Thus, terms written as "[group]oxy" refer to a particular group when linked by oxygen, for example, the terms "alkoxy" or "alkyloxy", "alkenoxy" or "alkenyloxy", "alkynoxy" or alkynyloxy", "aryloxy" and "acyloxy", respectively, denote alkyl, alkenyl, alkynyl, aryl and acyl groups as hereinbefore defined when linked by oxygen. Similarly, terms written as "[group]thio" refer to a particular group when linked by sulfur, for example, the terms "alkylthio", "alkenylthio", alkynylthio" and "arylthio", respectively, denote alkyl, alkenyl, alkynyl and aryl groups as hereinbefore defined when linked by sulfur.

[00160] The term "substituted" or "optionally substituted" is used to indicate that a group may have a substituent at each substitutable atom of the group (including more than one substituent on a single atom), provided that the designated atom's normal valency is not exceeded and the identity of each substituent is independent of the others. Combinations of substituents and/or variables are permissible only if such combinations result in stable compounds. The terms "stable compound" or "stable structure" mean a compound that is sufficiently robust to survive isolation to a useful degree of purity from a reaction mixture, and formulation into an efficacious agent.

[00161] The term "functionalized" with reference to any moiety refers to the presence of one or more functional groups in the moiety. Various functional groups can be introduced in a moiety by way of one or more functionalization reactions known to a person having ordinary skill in the art. Non-limiting examples of functionalization reactions include: alkylation, epoxidation, sulfonation, hydrolysis, amidation, esterification, hydroxylation, dihydroxylation, amination, ammonolysis, acylation, nitration, oxidation, dehydration, elimination, hydration, dehydrogenation, hydrogenation, acetalization, halogenation, dehydrohalogenation, Michael addition, aldol condensation, Canizzaro reaction, Mannich reaction, Clasien condensation, Suzuki coupling, and the like. In one non-limiting embodiment, the term "functionalized" with reference to any moiety refers to the presence of one more functional groups selected from the group consisting of alkyl, alkenyl, hydroxyl, carboxyl, halogen, alkoxy, amino, imino, and

combinations thereof, in the moiety.

[00162] The term "monomer" refers to a small molecule that chemically bonds during polymerization to one or more monomers of the same or different kind to form a polymer.

[00163] The term "polymer" refers to a large molecule comprising one or more types of monomer residues (repeating units) connected by covalent chemical bonds. By this definition, polymer encompasses compounds wherein the number of monomer units can range from very few, which more commonly can be called as oligomers, to very many. Non-limiting examples of polymers include homopolymers, copolymers, terpolymers, tetrapolymers and the higher analogues. The polymer can have a random, block, and/or alternating architecture.

[00164] The term "homopolymer" refers to a polymer that consists of a single monomer type.

[00165] The term "copolymer" refers to a polymer that comprises at least two different monomer types.

[00166] The term "terpolymer" refers to a copolymer that comprises three different monomer types.

[00167] The term "branched" refers to any non-linear polymer structure. The term includes both branched and hyper-branched structures.

[00168] The term "block copolymer" refers to a polymer comprising at least two blocks of polymerized monomers. Any block can be derived from either a single monomer resulting in a homopolymeric subunit, or two or more monomers resulting in a copolymeric (or nonhomopolymeric) subunit in the block copolymer. The block copolymers can be di block copolymers (i.e., polymers comprising two blocks of monomers), triblock copolymers (i.e., polymers comprising three blocks of monomers), multiblock copolymers (i.e., polymers comprising more than three blocks of monomers), and combinations thereof. The block copolymers can be linear, branched, star or comb like, and have structures such as [A][B], [A][B][A], [A][B][C], [A][B][A][B], [A][B][C][B], etc. An exemplary representation of block copolymer is [A]x[B]y or [A]x[B]y[C]z, wherein x, y and z are the degrees of polymerization (DP) of the corresponding blocks [A], [B] and [C]. Additional insight into the chemistry, characterization and applications of block copolymers can be found in the book 'Block Copolymers: Synthetic Strategies, Physical Properties, and Applications', by Nikos Hadjichristidis, Stergios Pispas, and George Floudas, John Wiley and Sons (2003), the contents of which are herein incorporated in its entirety by reference.

[00169] The terms “reversible deactivation radical polymerization” (RDRP), "controlled radical polymerization" or “controlled/living radical polymerization” refer to a specific radical polymerization process, also denoted by the term of "living radical polymerization", in which use is made of control agents, such that the polymer chains being formed are functionalized by end groups capable of being reactivated in the form of free radicals by virtue of reversible transfer or reversible termination reactions, thus enabling synthesis of e.g. block copolymers.

[00170] The term "addition-fragmentation" refers to a two-step chain transfer mechanism during polymerization wherein a radical addition is followed by fragmentation to generate a new radical species.

[00171] The term "residue of at least one crosslinker" refers to one or more cross-linking moieties that become a part of the polymer backbone after polymerization. The residue can be mono-, di- or polyvalent.

[00172] The term " radical addition polymerization initiator" refers to a compound used in a catalytic amount to initiate a radical addition polymerization. The choice of initiator depends mainly upon its solubility and its decomposition temperature.

[00173] The term "alkyl acrylate" refers to an alkyl ester of an acrylic acid or an alkyl acrylic acid.

[00174] The term "alkyl acrylamide" refers to an alkyl amide of an acrylic acid or an alkyl acrylic acid.

[00175] The term "moiety" refers to a part or a functional group of a molecule.

[00176] The term "pharmaceutical composition" refers to any composition comprising at least one pharmaceutically active ingredient, as well as any product which results, directly or indirectly, from combination, complexation, or aggregation of any two or more of the ingredients, from dissociation of one or more of the ingredients, or from other types of reactions or interactions of one or more of the ingredients.

[00177] The term "coating composition" refers to an aqueous-based or solvent-based liquid composition that can be applied to a substrate and thereafter solidified (for example, by radiation, air curing, post-crosslinking or ambient temperature drying) to form a hardened coating on the substrate.

[00178] The term "degree of polymerization" (DP) as used herein generally refers to the

mean number-average degree of polymerization, as would be readily understood by those skilled in the art.

DETAILED DESCRIPTION

[00179] The skilled addressee will understand that the invention comprises the embodiments and features disclosed herein as well as all combinations and/or permutations of the disclosed embodiments and features.

EXAMPLES

[00180] The present invention will now be described with reference to the following examples which should be considered in all respects as illustrative and non-restrictive.

Materials

[00181] Acrylic acid ('AA', 99%, Sigma-Aldrich), poly(ethylene glycol) methyl ether acrylate ('PEGA', with 9 ethylene glycol units on average, M_n = 480 g mol^{-1}, Sigma-Aldrich), 4,4'-azobis-(4-cyanopentanoic acid) ('ACPA', 98%, Aesar), sodium bicarbonate ('$NaHCO_3$', Sigma-Aldrich), 1,3,5-trioxane (99%, Sigma-Aldrich), diethyl ether (100%, Chem Supply), ethanol (EtOH, 100%, Chem Supply), tetrahydrofuran ('THF', 100%, RCL Labscan), poly(ethylene glycol) diacrylate ('PEGDA', with 3 ethylene glycol units on average, M_n = 250 g mol^{-1}, Sigma-Aldrich), and ethylene glycol diacrylate ('EGDA', 90%, Sigma-Aldrich) were used as received. Inhibitors in styrene ('S', 99%, Sigma-Aldrich), *n*-butyl acylate ('*n*BA', 99%, Sigma-Aldrich), methyl methacrylate ('MMA', 99%, Sigma-Aldrich), benzyl methacrylate ('BzMA', 99%, Sigma-Aldrich) and 2-ethylhexyl methacrylate ('EHMA', 99%, Sigma-Aldrich) were removed by passing through an aluminum oxide column before use. Azobis(isobutyronitrile) ('AIBN', Sigma-Aldrich) in acetone was precipitated in water. Water was deionized before use (milli-Q water). The RAFT agent 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid ('DDMAT') and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid ('CPADB') were synthesized according to the literature.

Two-step synthesis of P(AA-*stat*-PEGA)-*b*-P(S-*stat*-*n*BA) amphiphilic block copolymers

[00182] The experiments are labelled A-x, B-x, C-x, D-x, E-x, and F-x (x is the experiment number). Entries A-x is RAFT aqueous emulsion polymerization of styrene and *n*BA performed at different pHs. Entries B-x is RAFT aqueous emulsion polymerization of styrene and *n*BA performed at pH 5 with different molar ratios [hydrophobic monomer]:[macroRAFT] (Scheme

1). Entries C-x, D-x, E-x, and F-x refer to synthesis of crosslinked P(AA-*stat*-PEGA)-*b*-P(S-*stat*-*n*BA) nanofibers (Scheme 2).

Synthesis of P(AA-*stat*-PEGA)-DDMAT macroRAFT agent

[00183] MacroRAFT agent was prepared by solution copolymerization of AA (0.8882 g, 12.3 mmol) and PEGA (5.9164 g, 12.3 mmol) (molar ratio = 50/50) using EtOH (5.0309 g) as a solvent in the presence of DDMAT RAFT agent (0.2 g, 0.55 mmol) (monomers/RAFT agent molar ratio = 44), ACPA (0.0154 g, 0.055 mmol). In addition, 1,3,5-trioxane (0.1650 g, 1.8 mmol) was added to the polymerization mixture as an internal reference for ^{1}H NMR analysis. The solution was mixed in a 25 mL glass vial at ambient temperature for 10 min, and subsequently purged for 30 min with nitrogen in an ice bath. Polymerization was carried out at 70°C in an oil bath with a stirring speed of 500 rpm for 3 h. The final overall conversion of AA and PEGA was 95% as determined by ^{1}H NMR. The obtained final polymerization mixture was added dropwise into 35 mL of diethyl ether in a 50 mL centrifuge tube, and centrifuged at 7000 rpm for 5 min. The product was precipitated in diethyl ether after centrifugation, and the supernatant was discarded. Then, it was re-filled with 35 mL of fresh diethyl ether and mixed well before centrifugation. This process was repeated three times. The purified samples were dried overnight in a vacuum oven at 50°C.

RAFT aqueous emulsion polymerization of styrene and *n*BA ([styrene]$_0$/[*n*BA]$_0$ = 70/30) (*Entries* A-x and B-x)

[00184] P(AA-*stat*-PEGA)-*b*-P(S-*stat*-*n*BA) amphiphilic block copolymers were prepared by RAFT-mediated aqueous emulsion polymerization of styrene and *n*BA ([styrene]$_0$/[*n*BA]$_0$ = 70/30). In this example, ACPA, $NaHCO_3$, P(AA-*stat*-PEGA)-DDMAT, and milli-Q water were added into a 25 mL glass vial. The solution was mixed using a sonication bath for 10 min. Different amounts of 1 M NaOH were added in *Entries* A-x to observe the effect of the pH. For A-1, pH of the solution was not adjusted (0 µL of 1M NaOH). For A-2 and A-3, 1 M NaOH solution was added to adjust the pH (290 µL of 1 M NaOH was added for A-2, and 930 µL for A-3). To the solution was added styrene and *n*BA ([hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 200) after pH adjustment. The effect of DP on hydrophobic block was explored in *Entries* B-x. The pH of the solution was adjusted to pH 5 by adding 290 µL of 1 M NaOH. Styrene and *n*BA with different [hydrophobic monomer]$_0$/[macroRAFT]$_0$ was added to the solution after adjusting the pH. Polymerization was carried out at 80°C in an oil bath with a stirring speed of 350 rpm for 6 h (*Entries* A-x) and 4 h (*Entries* B-x). The polymerization mixture was subsequently quenched by putting the flask in an ice bath. The conversion of styrene and *n*BA was determined by

gravimetric analysis. All experiments are summarized in Table 1 (*Entries* A-x) and Table 2 (*Entries* B-x).

[00185] The theoretical number-average molecular weight ($M_{n,th}$) was determined by eqn (1):

$$M_{n,th}=M_{macroRAFT}+\frac{(X_{conv.}\cdot[styrene]_0\cdot M_S)+(X_{conv.}\cdot[nBA]_0\cdot M_{nBA})}{[macroRAFT]_0} \quad (1)$$

[00186] where $M_{macroRAFT}$, M_S, M_{nBA} are the molar masses of macroRAFT agent, styrene, and *n*BA, respectively, $[macroRAFT]_0$, $[styrene]_0$, $[nBA]_0$ are the initial concentrations of macroRAFT agent, styrene, and *n*BA, respectively, and $X_{conv.}$ denotes total monomer conversion determined by gravimetry.

Synthesis of crosslinked P(AA-*stat*-PEGA)-*b*-P(S-*stat*-*n*BA) nanofibers ($[styrene]_0/[nBA]_0$ = 70/30) (*Entries* C-x, D-x, E-x, and F-x)

[00187] Crosslinked P(AA-*stat*-PEGA)-*b*-P(S-*stat*-*n*BA) nanofibers were synthesized by *in-situ* chemical crosslinking using the crosslinker EGDA (170.16 g mol^{-1}) or PEGDA (M_n = 250 g mol^{-1}) as a crosslinker. Two different approaches were used – the first approach was to introduce EGDA prior to the RAFT aqueous emulsion polymerization of styrene and *n*BA, whereas the second approach was to introduce EGDA after 2 h of polymerization (conversion > 90%). The ratio $[hydrophobic\ monomer]_0/[macroRAFT]_0$ was fixed at 100. After polymerization, 120 µL of the latex was added to 1 mL of THF (volume ratio ≈ 10/90) to observe whether the polymer particles dissolve in THF – insolubility indicates crosslinking has been achieved.

Synthesis of crosslinked P(AA-*stat*-PEGA)-b-P(S-*stat*-*n*BA) nanofibers ($[styrene]_0/[nBA]_0$ = 20/80) (*Entries* G-x, and H-x)

[00188] Synthesis was conducted as for RAFT aqueous emulsion polymerization of styrene and *n*BA described above, except that the styrene-to-*n*BA molar ratio was 20/80 ($[styrene]_0/[nBA]_0$ = 20/80), and nanoparticles were crosslinked by adding 5 mol% EGDA (relative to macroRAFT agent) after 2 h of polymerization. The pH of the solution was adjusted to pH 5 by adding 290 µL of 1 M NaOH for *Entries* G-x (Table SI-1) and 290 µL, 580 µL, and 870 µL of 1M NaOH for H-1, H-2, and H-3 (Table SI-2). Styrene and *n*BA with different $[hydrophobic\ monomer]_0/[macroRAFT]_0$ was added to the solution after adjusting the pH for *Entries* G-x. Styrene and *n*BA with different solids content at fixed ($[hydrophobic\ monomer]_0/[macroRAFT]_0$ = 130) was carried out for *Entries* H-x. The conversion of styrene

and *n*BA was determined by gravimetric analysis. Theoretical $M_{n,th}$ was determined by eqn (SI-1). All experiments are summarized in Table SI-1 (*Entries* G-x) and Table SI-2 (*Entries* H-x).

Gravimetric Analysis.

[00189] The total conversion of styrene and *n*BA was determined by gravimetric analysis. Latex at different time intervals were taken to observe progression of monomer conversion over time. 950 µL of the latex was weighed in a pre-weighed aluminium pan and dried in a 50°C vacuum oven overnight.

Nuclear Magnetic Resonance (NMR).

[00190] The final total conversion of AA and PEGA at t = 3 h was determined by ^{1}H NMR spectroscopy using a Bruker Avance III 300 MHz NMR with 1,3,5-trioxane used as an internal reference. Samples were prepared by dissolving 50 µL of the reaction mixture (t = 0 h and t = 3 h) in 600 µL of deuterated dimethyl sulfoxide (d_6-DMSO).

Gel Permeation Chromatography (GPC).

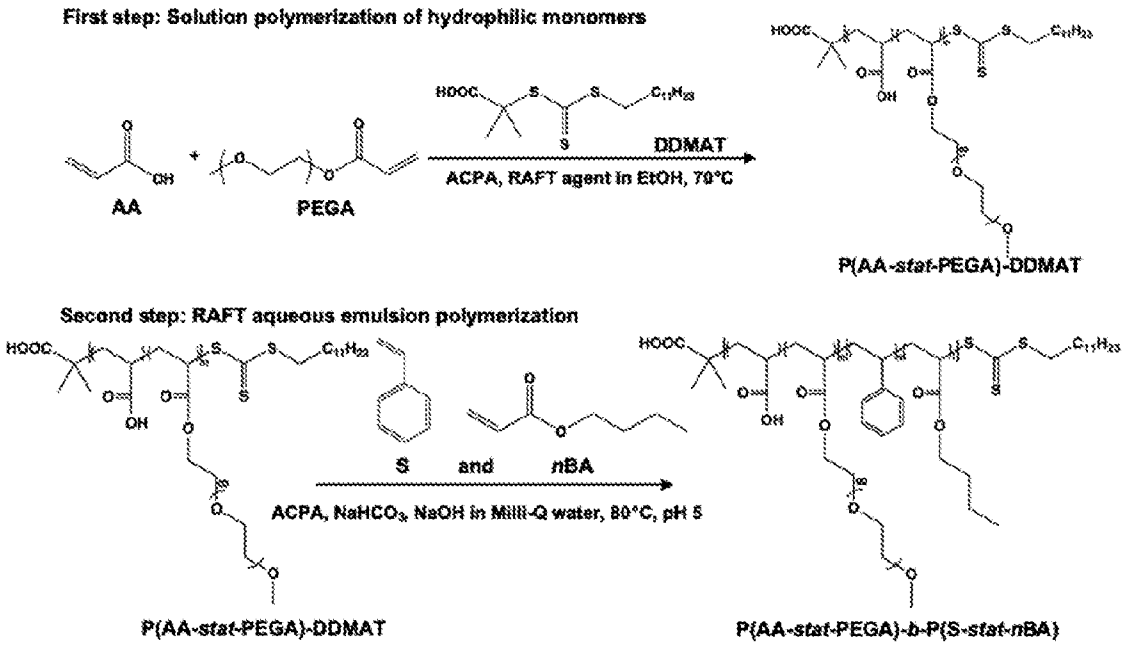
[00191] Number-average (M_n) and weight-average (M_w) molecular weights and dispersity ($Đ$) were determined by gel permeation chromatography (GPC) using a Shimadzu modular system, comprising an SIL-10AD autoinjector, an LC-10AT pump, a DGU-12A degasser, a CTO-10A column oven, and an RID-10A differential refractive index detector. A column arrangement consisting of a Polymer Laboratories 5.0 µm bead size guard column (50 × 7.8 mm), followed by four linear PL column (300 × 7.8 mm, 500, 10^3, 10^4, and 10^5 Å, 5 µm pore size) was used for the analysis. *N,N*-Dimethylacetamide (DMAc, 0.03% w/v LiBr, 0.05% w/v 2,6-dibutyl-4-methylphenol(BHT)) was used as the mobile phase at 50°C and flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear polystyrene standards ranging from 500 to 10^6 g mol^{-1} (Polymer Laboratories). Chromatograms were processed using Cirrus 2.0 software (Polymer Laboratories). Samples were methylated to modify the carboxylic group in acrylic acid to reduce the interaction with the column. The dried latex (10 mg) was added to 1 mL of milli-Q water in a 25 mL glass vial and HCl was added to adjust to pH 3-4. Then, 20 mL of THF was added to the mixture. Trimethylsilyldiazomethane methylating agent was added into the vial drop by drop. The mixture was stirred at room temperature for 4 h. After methylation, the solution was dried in an aluminium pan at ambient temperature overnight. It was further dried at 35°C using high vacuum oven for 1 h to remove water. Samples were dissolved in DMAc and filtrated using a syringe filter (0.45 µm) prior to injection into the GPC system.

Transmission Electron Microscopy (TEM).

[00192] TEM samples were prepared by dropping 10 μL of diluted latex (10 μL of latex in 1 mL of milli-Q water) on a glow-discharged formvar-coated copper grid, which was dried at ambient temperature. The grid was glow-discharged to modify the grid surface from hydrophobic to hydrophilic to avoid accumulation of block copolymer nanoparticles on the periphery of the grid. The TEM images were obtained under an accelerating voltage of 100 kV using a JEOL 1400 transmission electron microscope.

Effects of pH

[00193] PISA was conducted as an aqueous emulsion polymerization at 80 °C using the macroRAFT agent P(AA-*stat*-PEGA)-TTC (hydrophilic block; M_n = 13,400 g/mol; $Đ$ = 1.20) and ACPA as initiator (Scheme 1). In this example, the macroRAFT agent was prepared by solution polymerization in EtOH at 70 °C (Scheme 1, Fig. 9; M_n = 13,400 g/mol; $Đ$ = 1.20). Copolymerization of styrene and *n*BA at a weight ratio of 65.5:34.5 (corresponding to a theoretical T_g value of 27.1 °C at full conversion based on the Fox Equation) in RAFT aqueous emulsion polymerization (*Entries* A-x) was carried out at three different pH (3.5, 5, and 7) to determine the most suitable pH for formation of nanofibers. The targeted degree of polymerization (DP) was fixed at [hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 200 (Table 1).



Scheme 1. RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent.

[00194] For all three pH values, the overall monomer conversion after 6 h reached over 90% with the highest conversion reached at pH 3.5 (Table 1, Fig. 1.). Without wishing to be bound by theory, it is believed the self-assembly behaviour itself can be influenced by the pH.

[00195] At pH 3.5, the molecular weight distribution (MWD) shifted towards higher molecular weight with low dispersity ($Đ$ = 1.18) indicating good control/livingness (Table 1, Fig. 2.). However, for pH 5 (Fig. 2. A-2) and pH 7 (Fig. 2. A-3), pronounced low molecular weight shoulders were present, consistent with unreacted macroRAFT agent remaining.

[00196] The TEM images show that only spherical morphologies were obtained at pH 3.5 (Fig. 3. A-1) and pH 7 (Fig. 3. A-3) with particle diameters of approximately 50 nm and 120 nm, respectively. However, a mixture of nanofibers and vesicles was obtained at pH 5 (Fig. 3. A-2). It is contemplated that at pH 3.5, it is possible that due to the protonation of the AA units of the macroRAFT, this block became sufficiently hydrophobic for segments to be buried within particles, hence not driving reorganization into higher order morphologies. Moreover, reduced segregation strength between macroRAFT agent (hydrophilic block) and core-forming block (hydrophobic block) due to the absence of charges on macroRAFT agent could have led to spherical morphology being favored. Formation of spherical micelles without higher order morphologies has been reported previously for the copolymerization of styrene and MMA using poly(methacrylic acid-*stat*-poly(ethylene oxide) methyl ether methacrylate) at pH 3.5. It is contemplated that at pH 5, partial ionization of the hydrophilic block would minimize the occurrence of AA moieties being buried within the particles, thus resulting in transformation into nanofibers/vesicles as the hydrophobic block length was sufficiently long. Without wishing to be bound by theory, the spherical morphology obtained at pH 7 can presumably be rationalized by negative charges generated by deprotonation of AA hindering the reorganization of spheres into higher order morphology by electrostatic repulsion.

Table 1. Experimental conditions and results of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent at 80 °C, molar ratio AA/PEGA = 50/50, styrene/*n*BA = 70/30, [macroRAFT]$_0$ = 6.2 mmol/L, [hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 200, [$NaHCO_3$]$_0$/[ACPA]$_0$ = 3.5.

#	pH	t (h)	Conv.[a] (%)	$M_{n,th}$[b]	M_n[c]	$Đ$[d]	Solids content[e] (%)
A-1	3.5	6	95	32,900	29,900	1.18	17.6
A-2	5	6	94	32,700	21,000	1.76	17.5
A-3	7	6	91	32,000	44,900	2.13	17.5

[a] Monomer conversion by gravimetry.

[b] $M_{n,th}$ calculated using monomer conversion via eqn (1).

[c] Experimental M_n determined by GPC in DMAc.

[d] Dispersity index M_w/M_n determined by GPC in DMAc.

[e] Solids content in wt% based on overall weight of latex.

Effects of DP of hydrophobic block

[00197] Polymerizations were subsequently carried out at various [hydrophobic monomer]$_0$/[macroRAFT]$_0$ at pH 5 with fixed macroRAFT agent concentration (*Entries* B-x, Table 2) with a view to obtaining pure nanofibers as opposed to mixed morphologies (as in Fig. 3. A-2). The targeted DP was varied from 50 to 200 with the solid content as a consequence increasing from 10 to 17.5 wt%. The color of the final dispersions changed from yellow to white as the amount of hydrophobic monomer was increased. The experimental M_n values were similar to $M_{n,th}$ with $Đ$ = 1.54-1.93 (Table 2). Low molecular weight shoulders in the MWDs existed in all cases demonstrating the presence of unreacted macroRAFT for the reasons discussed above (Fig. 4).

[00198] TEM imaging revealed that the morphology transformed from spheres (Fig. 5. B-1) to nanofibers (Fig. 5. B-2, and B-3) and finally to vesicles (Fig. 5. B-4, B-5, and B-6) with increasing target DP as expected. Without wishing to be bound by theory, it is believed that this arises because of an increase in the packing parameter (P) due to the increase in core-forming block length. The viscosity of the latex increased when nanofibers were obtained. All latexes remained stable without coagulation and sedimentation. Although nanofibers were observed over a wide range of DP from 100 to 200, the parameter window corresponding to relatively pure nanofibers was narrow. In most cases, nanofibers coexisted with small amounts of spheres (Fig.

5. B-2) or vesicles (Fig. 5. B-3 to B-6). The amount of vesicles increased as DP increased from 130 to 200. Relatively pure nanofibers were obtained at DP = 100 (Fig. 5. B-2) and 130 (Fig. 5. B-3).

[00199] Narrower MWD was achieved with decreasing target DP, when spheres (Fig. 5. B-1, Đ = 1.54) or relatively pure nanofibers (Fig. 5. B-2, Đ = 1.56) were obtained (Table 2 and Fig. 4.). Higher dispersity was observed with the mixture of nanofibers and vesicles (Fig.5. B-3 to B-6) leading to broader MWD. In previous reports, similar results have been reported on homopolymerization of styrene in the presence of hydrophilic macroRAFT agent in RAFT aqueous emulsion polymerization.

Table 2. Experimental conditions and results of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA) macroRAFT agents at 80 °C, pH 5, molar ratio AA/PEGA = 50/50, styrene/*n*BA = 70/30, [macroRAFT]$_0$ = 6.2 mmol/L, [NaHCO$_3$]$_0$/[ACPA]$_0$ = 3.5.

#	DP	t (h)	Conv.[a] (%)	$M_{n,th}$[b] (g/mol)	M_n[c] (g/mol)	$Đ$[d]	Solids content[e] (%)
B-1	50	4	85	17,400	17,300	1.54	10.0
B-2	100	4	90	21,900	23,800	1.56	12.6
B-3	130	4	88	24,600	23,400	1.74	14.1
B-4	150	4	90	26,900	27,800	1.67	15.1
B-5	170	4	95	29,300	27,600	1.93	16.1
B-6	200	4	90	31,900	29,700	1.86	17.5

[a] Monomer conversion by gravimetry.

[b] Theoretical $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (1).

[c] Experimental M_n determined by GPC in DMAc.

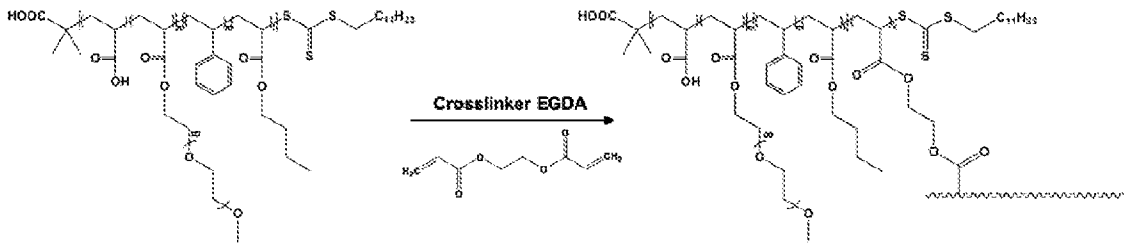
[d] Dispersity index (M_w/M_n) determined by GPC in DMAc.

[e] Solids content in wt% based on total weight.

Synthesis of crosslinked nanofibers ([styrene]$_0$/[*n*BA]$_0$ =70/30)

[00200] Polymeric nanofibers prepared by PISA can be crosslinked using a variety of approaches. In one example, in the present invention divinyl crosslinkers EGDA and PEGDA were utilised to crosslink the core-section of the nanofibers (Scheme 2). Two simple *in-situ* crosslinking methods were explored: (*i*) addition of the crosslinker at the beginning of the

emulsion polymerization (*Entries* C-x and D-x), and (*ii*) addition of the crosslinker after 2 h of polymerization (conversion > 90%) (*Entries* E-x and F-x). Different crosslinked structures would be expected depending on the crosslinking method. The entire core-forming block would be crosslinked based on method (*i*), while the core-forming block would only be partially crosslinked using method (*ii*) (only the part of the block forming at the highest conversion range. *i.e.* the segment of the chain nearest the RAFT end group).



Scheme 2. Schematic representation crosslinking step of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA)-TTC macroRAFT agent using EGDA or PEGDA as crosslinker ([hydrophobic monomers]$_0$/[macroRAFT]$_0$ = 100, pH 5).

[00201] The base conditions without crosslinker correspond to TEM image B-2 (Fig. 5), which yielded relatively pure nanofibers in the absence of crosslinkers ([hydrophobic monomer]$_0$/[macroRAFT]$_0$ = 100). When added at the beginning of the polymerization (Method (*i*)), EGDA and PEGDA (*Entries* C-x, and D-x) interfered with the PISA process, affecting the final morphology. In the case of PEGDA, thinner (Fig. 6; C-2) and shorter (Fig. 6; C-3) nanofibers were obtained with 1 or 2.5 mol% PEGDA. In the case of EGDA (*Entries* D-x), relatively pure nanofibers (Fig. 6; D-1, and D-2) were obtained with 0.5 or 1 mol% EGDA whereas spherical micelles were obtained when 10 mol% EGDA was introduced (Fig. 6; D-3). Without wishing to be bound by theory, it is believed that crosslinking influences the final morphology.

[00202] When added after 2 h of polymerization (Method (*ii*)), EGDA and PEGDA (*Entries* E-x, and F-x) exerted relatively less influence on the final morphology than for Method (*i*), except for 10 mol% EGDA. Again, near pure nanofibers were obtained without crosslinker (Fig 6. B-2). In the case of PEGDA, nanofibers and a small amount of vesicles were obtained for 1 and 10 mol% PEGDA (Fig. 6; E-2 and E-3). Relatively pure nanofibers were obtained for 3 and 5 mol% EGDA (Fig. 6; F-1 and F-2). However, 10 mol% EGDA resulted in the formation of

vesicles (Fig. 6; F-3). Crosslinked nanofibers/vesicles may be obtained by introducing crosslinker at the beginning of polymerization (Method (*i*)) and delaying the introduction of crosslinker (Method (*ii*)) once the desired morphology has been formed.

[00203] The nanoparticle latexes were mixed with THF to confirm crosslinking. THF is a good solvent for the linear diblock copolymer, *i.e.* transparent solutions indicate minimal (if any) crosslinking, whereas turbid solutions are consistent with significant crosslinking. Near pure nanofibers were obtained when 3 and 5 mol% EGDA was introduced at $t = 2$ h (Method (*ii*)) (Fig.6; F-1, and F-2). Addition of THF to these latexes resulted in turbid solutions (Fig. 7; (d)), confirming successful crosslinking. When added at $t = 0$ h (Method (*i*)), crosslinking was successful in all cases for both EGDA and PEGDA, as turbid solutions (Fig. 7; (a), and (b)) were observed in all cases. When added at $t = 2$ h (Method (*ii*)), crosslinking was successful with EGDA (Fig. 7; (d)), whereas PEGDA did not result in significant crosslinking as evidenced by transparent solutions on addition of THF (Fig. 7; (c)).

[00204] EGDA and PEGDA behaved differently as determined by dissolving the final dispersions in THF (Fig. 7) – crosslinking was successful for EGDA when added at $t = 0$ h or $t = 2$ h (Method (*i*) and (*ii*)), whereas PEGDA only resulted in successful crosslinking when added at $t = 0$ h (Method (*i*)). Without wishing to be bound by theory, a possible explanation can be the difference in hydrophobicity between these crosslinkers. The crosslinkers would initially be present as droplets in the continuous phase, and gradually diffuse into the polymer particles as polymerization progresses in accordance with an emulsion polymerization mechanism. Due to the higher hydrophilicity (higher water solubility) of PEGDA, it is possible that excessive partitioning to the aqueous phase limited the extent of crosslinking.

[00205] Overall, it can be concluded that 1 mol% EGDA added at $t = 0$ h by using Method (*i*) or 3 and 5 mol% EGDA added at $t = 2$ h by using Method (*ii*) are the best method to achieve crosslinked nanofibers.

Synthesis of crosslinked nanofibers ($[\text{styrene}]_0/[n\text{BA}]_0 = 20/80$)

[00206] Polymeric nanoparticles with T_g of the core-forming block below 0 °C were synthesized by copolymerization of styrene and *n*BA at a weight ratio of 16.9:83.1 (corresponding to a theoretical T_g value of -37.6 °C at full conversion based on the Fox Equation) based on the methodology in Schemes 1 and 2. Crosslinking was achieved by introducing 5 mol% EGDA after 2 h of polymerization (conversion > 90%) (Method (*ii*)). Structural stability despite the low T_g of the base polymer was achieved by crosslinking, thereby

enabling TEM imaging without the need for cryoTEM.

[00207] Polymerizations were first conducted by varying [hydrophobic monomer]$_0$/[macroRAFT]$_0$ at a fixed macroRAFT agent concentration ([macroRAFT]$_0$ = 6.2 mmol/L) at pH 5 targeting nanofibers (*Entries* G-x, Table SI-1). The targeted DP was varied from 80 to 300 with the solids content increasing from 12.2% to 23.5%. In all cases, monomer conversion was over 90% (Table SI-2). The morphology changed from spheres (Fig. 10; G-1, G-2, and G-3) to nanofibers (Fig. 10; G-4) and finally to vesicles (Fig. 10; G-8, and G-9) with increasing targeted DP. Nanofibers were observed over the range of targeted DP from 130 to 180 (Fig. 10). In most cases, nanofibers coexisted with vesicles, and the amount of vesicles increased with increasing DP (Fig. 10; G-5, G-6, G-7, G-8, and G-9). Nanofibers with a small amount of spheres and vesicles were obtained at DP = 130 (Fig. 10; G-4). The final dispersions were stable without sedimentation or coagulation, and the viscosity increased with increasing amount of nanofibers as expected. The final dispersions (*Entries* G-x) were dissolved in THF, resulting in turbid solutions in all cases indicating successful crosslinking.

[00208] Nanofibers with spheres and vesicles were obtained at DP = 130 (Fig. 10; G-4) as mentioned above when the solids content was 15.2% ([macroRAFT]$_0$ = 6.2 mmol/L). The solids content was subsequently further increased to 24.7% ([macroRAFT]$_0$ = 11.5 mmol/L), and 32.7% ([macroRAFT]$_0$ = 17.7 mmol/L) while the targeted DP was fixed at 130 (*Entries* H-x, Table SI-2). Monomer conversion was over 90% in all cases (Table SI-2) and the resulting latexes were stable. Near pure nanofibers were formed when the solids content was 24.7% (Fig. 8. H-2), but a large amount of spheres with few nanofibers resulted at 32.7% (Fig. 8. H-3). Turbid solutions were obtained (*Entries* H-x) in THF, indicating successful crosslinking.

Conclusions

[00209] As shown herein, PISA implemented as aqueous RAFT emulsion polymerization has been utilised for synthesis of nano-sized polymeric fibers of low T_g using the macroRAFT agent P(AA-*stat*-PEGA)-TTC. However, it will be appreciated that different types of macroRAFT agents can be used as alternatives. As shown above, two types of nanofibers were prepared with the core-forming block consisting of different molar ratios S : *n*BA, namely 70:30 and 20:80, corresponding to theoretical glass transition temperatures of 27.1 °C (S : *n*BA = 70 : 30) and -37.6 °C (S : *n*BA = 20 : 80). In preferred embodiments that produced a high yield of nanofibers, the pH was 5. Additionally, preferred embodiments utilised crosslinking of the core-block using the divinyl monomers poly(ethylene glycol) diacrylate (PEGDA) and ethylene glycol diacrylate (EGDA), respectively, that were introduced either at the beginning of the PISA process or

towards the end of the growth of the core-forming block. The nature of the crosslinker and the time of addition can influence the nanofiber morphology. In preferred embodiments, addition of the crosslinker at the beginning or late in the polymerization maintained nanofiber morphology while crosslinking successfully.

Supplemental information

[00210] **Table SI-1.** Experimental conditions and results of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA) macroRAFT agent at 80 °C, pH 5, molar ratio AA/PEGA = 50/50, styrene/*n*BA = 20/80, EGDA/macroRAFT = 5/1, $[\text{macroRAFT}]_0 = 6.2$ mmol/L, $[NaHCO_3]_0/[\text{ACPA}]_0 = 3.5$.

#	DP	t (h)	Conv.[a] (%)	$M_{n,th}$[b] (g/mol)	Solids content[c] (%)
G-1	80	4	100	22,300	12.2
G-2	100	4	100	24,600	13.4
G-3	115	4	98	26,300	14.2
G-4	130	4	100	28,800	15.2
G-5	150	4	100	30,800	16.1
G-6	180	4	100	34,500	17.9
G-7	200	4	96	35,900	18.7
G-8	250	4	94	41,200	21.1
G-9	300	4	93	46,600	23.5

[a] Monomer conversion by gravimetry.

[b] $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (SI-1).

[c] Solids content in wt% based on overall weight of latex.

[00211] The theoretical number-average molecular weight ($M_{n,th}$) was determined by **eqn (SI-1)**:

$$M_{n,th} = M_{\text{macroRAFT}} + \frac{(X_{conv.} \cdot [\text{styrene}]_0 \cdot M_S) + (X_{conv.} \cdot [n\text{BA}]_0 \cdot M_{n\text{BA}}) + (X_{conv.} \cdot [\text{EGDA}]_0 \cdot M_{\text{EGDA}})}{[\text{macroRAFT}]_0} \quad \text{(SI-1)}$$

Table SI-2. Experimental conditions and results of RAFT aqueous emulsion polymerization of styrene and *n*BA in the presence of P(AA-*stat*-PEGA) macroRAFT agent at 80 °C, pH 5, molar

ratio AA/PEGA = 50/50, styrene/*n*BA = 20/80, EGDA/macroRAFT = 5/1, $[macroRAFT]_0 = 6.2$ mmol/L, $[NaHCO_3]_0/[ACPA]_0 = 3.5$.

#	DP	t (h)	Conv.[a] (%)	$M_{n,th}$[b] (g/mol)	Solids content[c] (%)
H-1	130	4	100	28,800	15.2
H-2	130	4	100	28,300	24.7
H-3	130	4	91	26,800	32.7

[a] Monomer conversion by gravimetry.

[b] $M_{n,th}$ calculated using monomer conversion obtained from gravimetry via eqn (SI-1).

[c] Solids content in wt% based on overall weight of latex.

[00212] **Example SI-1.** In this example, block copolymers comprising hydrophobic monomers were prepared via dispersion polymerization. Previous works have shown PISA can be conducted in non-polar solvent such as dodecane and mineral oil using hydrophobic monomers. However, such non-polar solvents have usually high boiling point and are difficult to remove. Herein, we describe the preparation of hydrophobic block copolymer in a mixture of water and alcohol. In a preferred embodiment, the hydrophobic monomer is substantially insoluble in water and/or substantially soluble in an 80/20 vol% ethanol/water mixture.

Synthesis of PMMA-CPADB macroRAFT agent

[00213] MacroRAFT agent was prepared by solution polymerization of MMA (6.0926 g; 60.8 mmol) using toluene (6.0 g) as a solvent in the presence of CPADB RAFT agent (0.2 g; 0.72 mmol; monomers/RAFT agent molar ratio = 85), AIBN (0.0117 g; 0.07 mmol; CPADB/AIBN molar ratio = 10.0). The solution was mixed in a 25 mL glass vial at ambient temperature for 10 min, and subsequently purged for 30 min with nitrogen in an ice bath. Polymerization was carried out at 70 °C in an oil bath with a stirring speed of 500 rpm for 20 h. The final conversion of MMA was 78% as determined by ^1H NMR. The final polymerization mixture was added dropwise into 35 mL of diethyl ether in a 50 mL centrifuge tube, and centrifuged at 7000 rpm for 5 min. The precipitated product was collected after centrifugation, and the supernatant was discarded. The product was redissolved in toluene after precipitation, and subsequently added dropwise into 35 mL of fresh diethyl ether and mixed well before centrifugation. This process was repeated three times. The purified samples were dried overnight in a vacuum oven at 50°C. THF GPC analysis using a refractive index detector and poly(methyl methacrylate) standards indicated an M_n of 8,200 g mol^{-1} and M_w/M_n of 1.17.

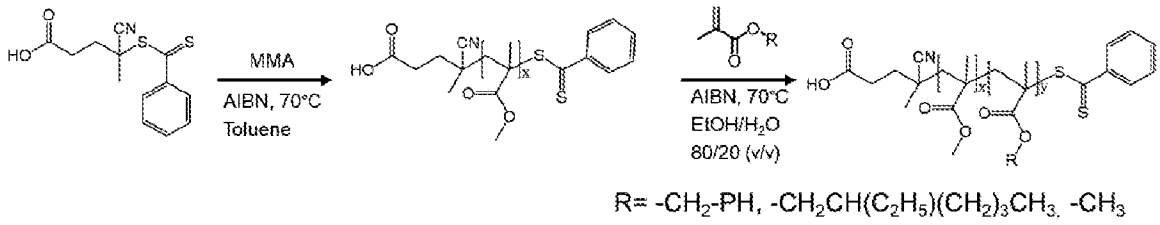
RAFT dispersion polymerization of EHMA and MMA ($[EHMA]_0/[MMA]_0$ = 90/10)

[00214] PMMA-*b*-P(EHMA-*stat*-MMA) block copolymers were prepared by RAFT-mediated dispersion polymerization of EHMA and MMA ($[EHMA]_0/[MMA]_0$ = 90/10) in EtOH and milli-Q water mixture (EtOH/water = 80/20 v/v). The following example of PMMA-*b*-P(EHMA-*stat*-MMA) with targeted degree of polymerization (DP) 100 at 10% w/w solids is representative and conducted as follows. PMMA-CPADB (0.2624 g; 0.04 mmol), 1,3,5-trioxane (0.0477 g; 0.53 mmol), EtOH (6.3120 g), and milli-Q water (2.0 g) were weighed into a 25 mL glass vial. 1,3,5-trioxane was added as an internal reference to determine the monomer conversion by ^{1}H NMR. The solution was stirred in a preheated oil bath at 70 °C for 10 min. Then, EHMA (0.6299 g; 3.18 mmol), MMA (0.0353 g; 0.35 mmol), and AIBN (0.0029 g; 0.02 mmol; macroRAFT/AIBN = 2.0) were added into the solution, and subsequently purged for 30 min with nitrogen in an ice bath. Polymerization was carried out at 70 °C in an oil bath with a stirring speed of 300 rpm for 21 h.

RAFT dispersion polymerization of BzMA

[00215] PMMA-*b*-PBzMA block copolymers were prepared via dispersion polymerization of BzMA in the presence of PMMA-CPADB macroRAFT agent and AIBN in EtOH/water mixture. In this example, BzMA (0.4603 g, 2.6 mmol), PMMA-CPADB macroRAFT agent (0.4650 g, 0.065 mmol), AIBN (5.4 mg, 0.033 mmol) and 10 ml of EtOH/water mixture (80/20 by volume) were mixed in a 25 ml glass vial to give a [BzMA]:[RAFT]:[AIBN] molar ratio of 40:1:0.5. The mixture was purged with nitrogen gas for 30 min in an ice bath before placing in an oil bath at 70°C with magnetic stirring. After 18 h, the polymerization was stopped by removing from the oil and opened to the air. The monomer conversion was determined to be ~98% via ^{1}H NMR in d_6-DMSO. The as-synthesized block copolymers were analyzed by TEM/SEM.

[00216] Polymeric nanofibers comprising hydrophobic corona and core were synthesized via dispersion polymerization of hydrophobic monomers in EtOH and water mixture. Block polymers self-assembled to nanofibers and the morphologies were confirmed by TEM/SEM (Fig. 12).



Scheme SI-1. RAFT dispersion polymerization of hydrophobic monomer(s) in the presence of PMMA macroRAFT agent.

[00217] Although the invention has been described with reference to specific examples, it will be appreciated by those skilled in the art that the invention may be embodied in many other forms in particular features of any one of the various described examples may be provided in any combination in any of the other described examples. Various modifications and alterations to this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. It should be understood that this invention is not intended to be unduly limited by the illustrative embodiments and examples set forth herein and that such examples and embodiments are presented by way of example only with the scope of the invention intended to be limited only by the claims set forth herein as follows.

CLAIMS

1. A polymeric nanofiber having a core-shell morphology, wherein the shell is hydrophilic, and the core comprises:

a) a hydrophobic copolymer, or

b) a hydrophobic homopolymer having a Tg below 16°C.

2. An amphiphilic block copolymer comprising:

a block [A] comprising a hydrophilic homo- or copolymer; and

a block [B] comprising:

a) a hydrophobic copolymer having a Tg below about 75°C, or

b) a hydrophobic homopolymer having a Tg below 16°C;

and optionally a crosslinker.

3. The amphiphilic block copolymer of claim 2, when self-assembled into a nanofiber.

4. A method of producing the amphiphilic block copolymer of claim 2, the method comprising the steps of:

a) reacting at least one hydrophilic monomer using RDRP to form a hydrophilic block [A];

b) adding to hydrophilic block [A], a hydrophobic block [B] comprising at least one hydrophobic monomer using RDRP; and

c) optionally adding a crosslinker at step b).

5. The method of claim 4, further comprising a step, wherein the block copolymer self-assembles into a nanofiber of claim 1.

6. The method of claim 4 or 5, wherein the polymerization is conducted as RAFT, ATRP, or NMP.

7. The polymeric nanofiber of claim 1, the amphiphilic block copolymer of claim 2 or 3, or the method of any one of claims 4-6, wherein the hydrophillic block [A] is prepared from one or more of poly(ethylene glycol) methyl ether acrylate (PEGA), poly(ethylene glycol) methyl ether

methacrylate (PEGMA), and acrylic acid.

8. The polymeric nanofiber of claim 1, the amphiphilic block copolymer of claim 2 or 3, or the method of any one of claims 4-7, wherein the hydrophobic block [B] is prepared from one or more of styrene, n-butyl acrylate, methyl acrylate, and methyl methacrylate, preferably styrene, n-butyl acrylate (*n*BA), and tert-butyl acrylate (*t*BA).

9. The polymeric nanofiber of claim 1, the amphiphilic block copolymer of claim 2 or 3, or the method of any one of claims 4-6, wherein the hydrophobic block [B] comprises a hydrophobic copolymer selected to have a Tg of the hydrophobic block below about 75°C, preferably in the range of -70°C to 75°C.

10. The polymeric nanofiber of claim 1, the amphiphilic block copolymer of claim 2 or 3, or the method of any one of claims 4-6, wherein the hydrophobic block [B] comprises a hydrophobic homopolymer selected to have a Tg below 16 °C, preferably in the range of -70°C to 16°C.

11. The method of any one of claims 4-10, wherein the crosslinker is ethylene glycol diacrylate (EGDA) or poly(ethylene glycol) diacrylate (PEGDA).

12. The method of any one of claims 4-11, wherein the crosslinker at step c) is introduced either at the beginning of the polymerization or towards the end of the polymerization.

13. The method of any one of claims 4-12, wherein the polymerization is conducted at a pH in the range of about 3 to about 8, preferably at about 5.

14. The method of any one of claims 4-13, wherein the average degree of polymerization (DP) of the block copolymer is between about 50 and about 300.

15. The polymeric nanofiber of claim 1, amphiphilic block copolymer of claim 2 or 3, or the method of any one of claims 4-14, wherein the nanofiber has a width between about 1 nm and about 100 nm.

16. The polymeric nanofiber of claim 1, amphiphilic block copolymer of claim 2 or 3, or the method of any one of claims 4-15, wherein the nanofiber has a length between about 5 μm and

about 1000 μm.

17. A nanofiber when self-assembled from the amphiphilic block copolymer produced by the method of any one of claims 4 to 16.

18. Use of the nanofiber of any one of claims 1, 3, or 5-17 to at least partially produce a film or coating.

19. A method of forming the film or coating of claim 18, the method comprising the steps of:

dispersing the nanofiber of any one of claims 1, 3, or 5-17 in a solvent to form a dispersion;

applying the dispersion to a surface; and

allowing or causing the solvent to substantially or completely evaporate;

thereby forming said film.

20. Use of the nanofiber of any one of claims 1, 3, or 5-17 to prepare a composite material, comprising:

a matrix or binder; and

a nanofiber of any one of claims 1, 3, or 5-17 dispersed throughout the matrix or binder.

21. Use of the nanofiber of any one of claims 1, 3, or 5-17 to modify or improve the mechanical properties of a matrix or binder.

22. A method of producing a composite material, the method comprising the steps of:

providing a polymer dispersion;

dispersing the nanofiber of any one of claims 1, 3, or 5-17 in said polymer dispersion to form a mixture; and

drying the mixture so as to form the composite material.

23. A method of producing a composite material comprising a polymer and the nanofiber of any one of claims 1, 3, or 5-17 by melt extrusion, the method comprising the steps of:

heating a polymer and the nanofiber to a temperature greater than a melt temperature of the polymer;

mixing the polymer and the nanofiber; and

extruding the mixture to form the composite material.

24. Use of a polymeric nanofiber as a viscosity or rheology modifier, wherein the polymeric nanofiber comprises a core-shell morphology, wherein the shell is hydrophilic, and the core comprises a hydrophobic homopolymer or copolymer.

25. A method of producing a block copolymer, the method comprising the steps of:

a) reacting at least one hydrophobic monomer using RDRP to form a substantially hydrophobic block [A], wherein block [A] is substantially soluble in an 20/80 vol.% water / ethanol mixture;

b) adding to hydrophobic block [A], a hydrophobic block [B] comprising at least one hydrophobic monomer using RDRP wherein block [B] is more hydrophobic than block [A] and is a different composition to block [A]; and

c) optionally adding a crosslinker at step b).

26. The method of claim 25, further comprising a step wherein the block copolymer self-assembles into a nanofiber having a core-shell morphology.

27. The method of claim 25 or 26, wherein the hydrophobic block [A] substantially insoluble in water.

28. The method of any one of claims 25-27, wherein the polymerization is conducted as RAFT, ATRP, or NMP.

29. The method of any one of claims 26-28, wherein the block copolymer is prepared from one or more of benzyl methacrylate, ethyl hexyl methacrylate, and methyl methacrylate.

30. The method of claim 29, wherein the block copolymer is prepared from one or more of poly(methyl methacrylate) (PMMA), poly(benzyl methacrylate) (PBzMA), and poly(2-ethylhexyl methacrylate) (PEHMA).

31. The method of any one of claims 26-30, wherein the polar solvent is selected from the group consisting of water, methanol, ethanol, n-propanol isopropylalcohol, n-butanol, n-

pentanol, and mixtures thereof.

32. The method of any one of claims 26-31, wherein the nanofiber has a width between about 1 nm and about 100 nm.

33. The method of any one of claims 26-32, wherein the nanofiber has a length between about 0.5 μm and about 1000 μm.

34. A block copolymer comprising:

a hydrophobic block [A], wherein block [A] is substantially soluble in an 20/80 vol.% water / ethanol mixture; and

a hydrophobic block [B] comprising at least one hydrophobic monomer, wherein block [B] is more hydrophobic than block [A] and is a different composition to block [A];

and optionally a crosslinker.

35. A polymeric nanofiber having a core-shell morphology, wherein the shell is hydrophobic, and the shell comprises a polymer that is substantially soluble in an 20/80 vol.% water / ethanol mixture; and wherein the core is hydrophobic, and the core comprises a polymer that is more hydrophobic than the polymer of the shell, and is a different composition to the polymer of the shell.

36. Use of the block copolymer of claim 34 or the polymeric nanofiber of claim 35 to at least partially produce a film or coating.

37. Use of the block copolymer of claim 34 or the polymeric nanofiber of claim 35 to prepare a composite material, comprising:

a matrix or binder; and

a block copolymer of claim 34 or the polymeric nanofiber of claim 35 dispersed throughout the matrix or binder.

38. Use of the block copolymer of claim 34 or the polymeric nanofiber of claim 35 to modify or improve the mechanical properties of a matrix or binder.

39. Use of the block copolymer of claim 34 or the polymeric nanofiber of claim 35 as a viscosity or rheology modifier.

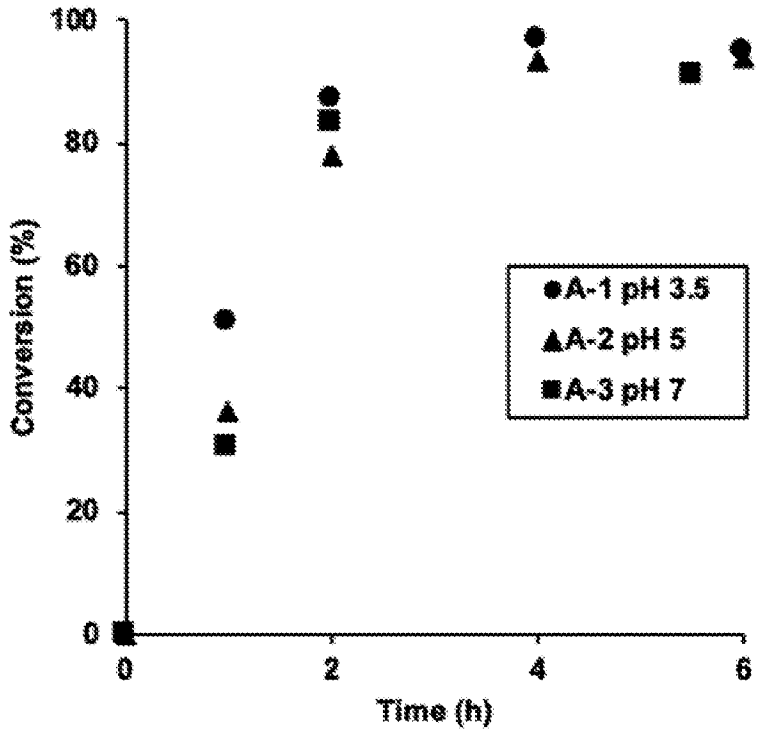


Figure 1

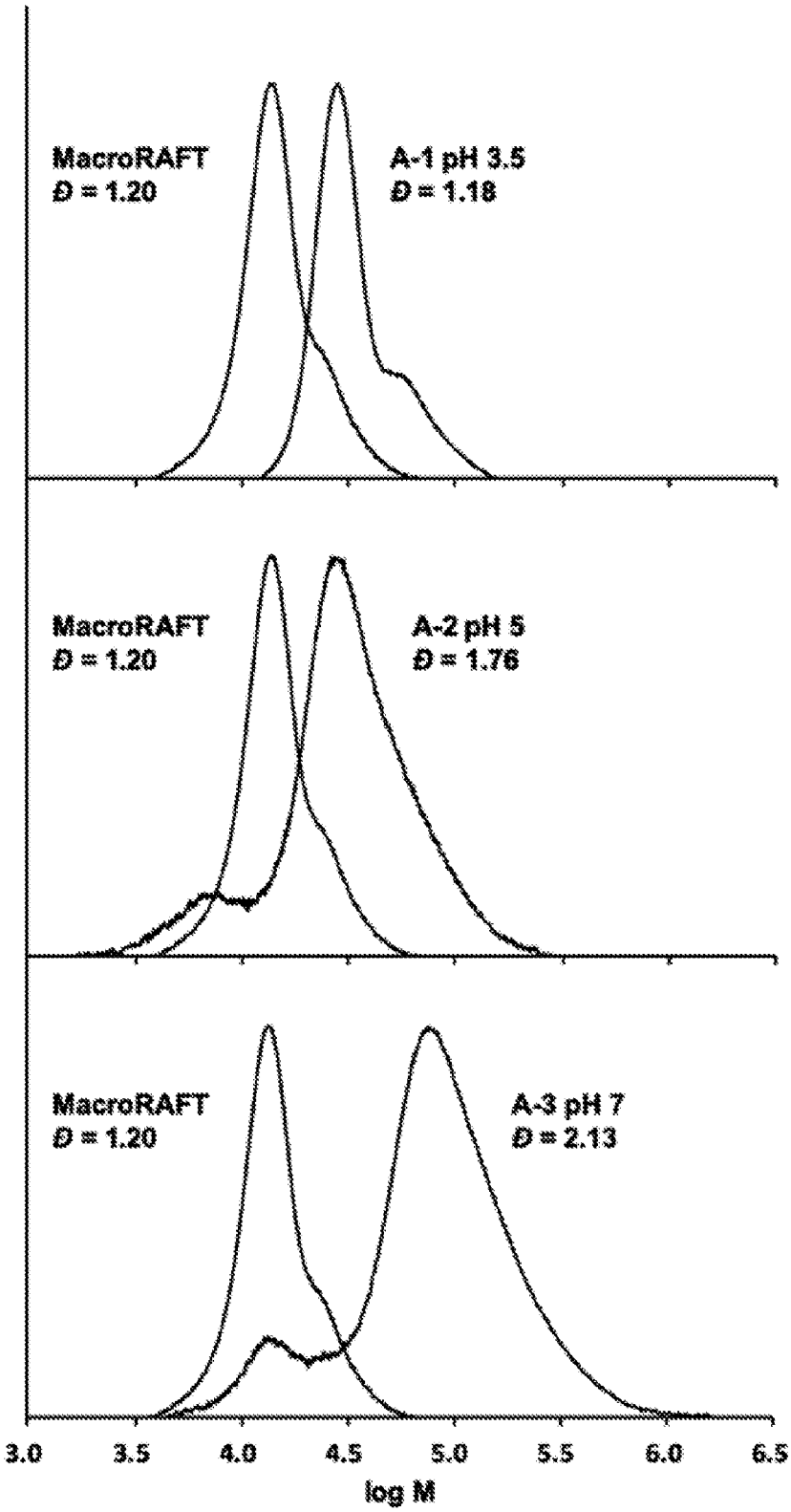

MacroRAFT
Đ = 1.20
A-1 pH 3.5
Đ = 1.18
MacroRAFT
Đ = 1.20
A-2 pH 5
Đ = 1.76
MacroRAFT
Đ = 1.20
A-3 pH 7
Đ = 2.13
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
log M

Figure 2

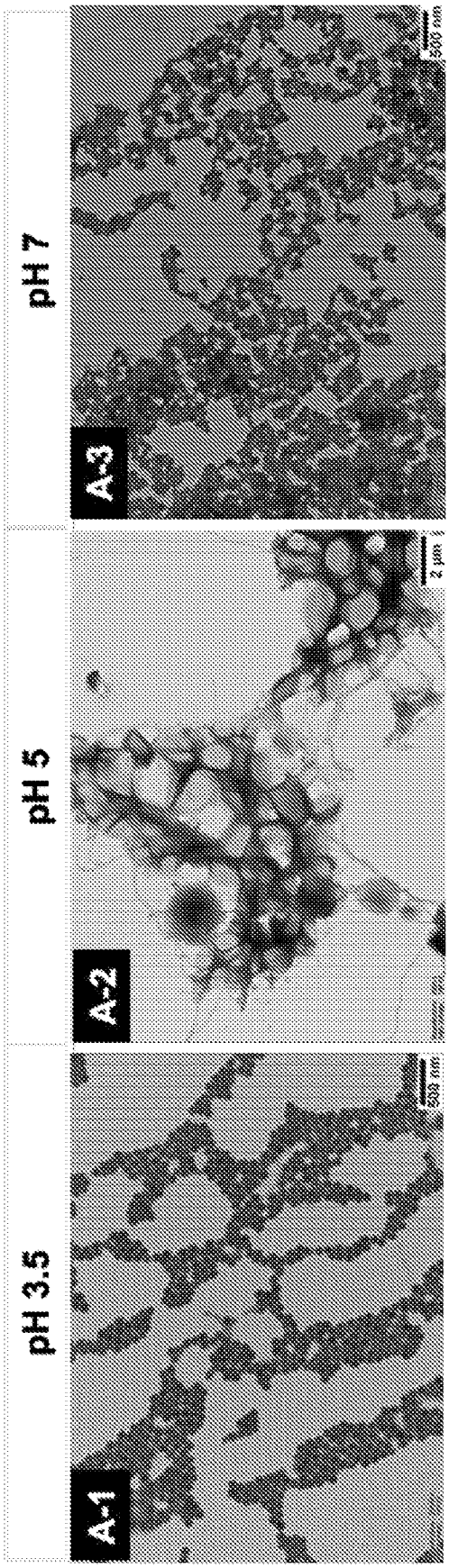


Figure 3

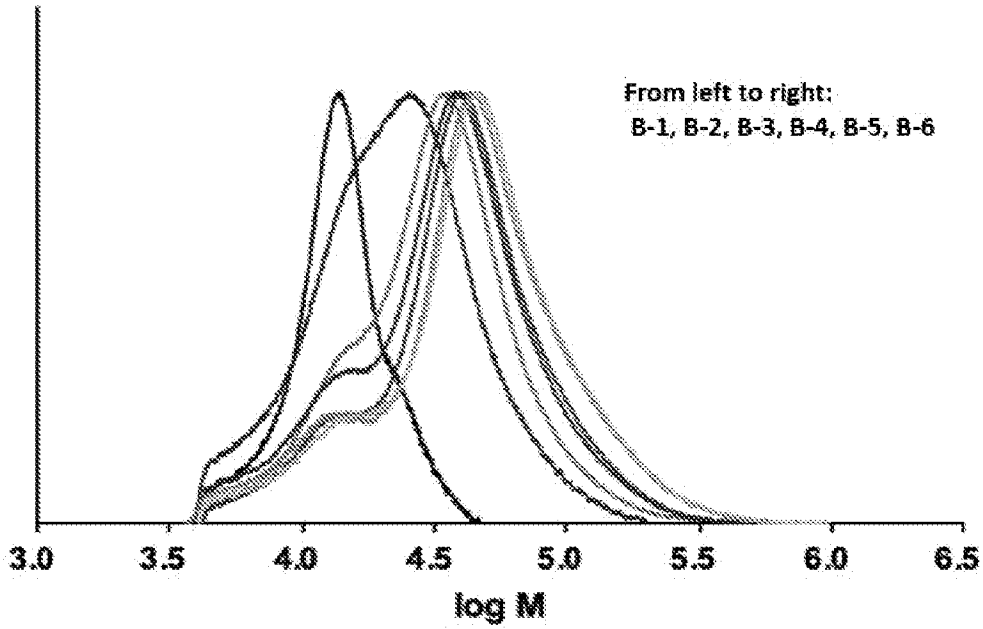


Figure 4

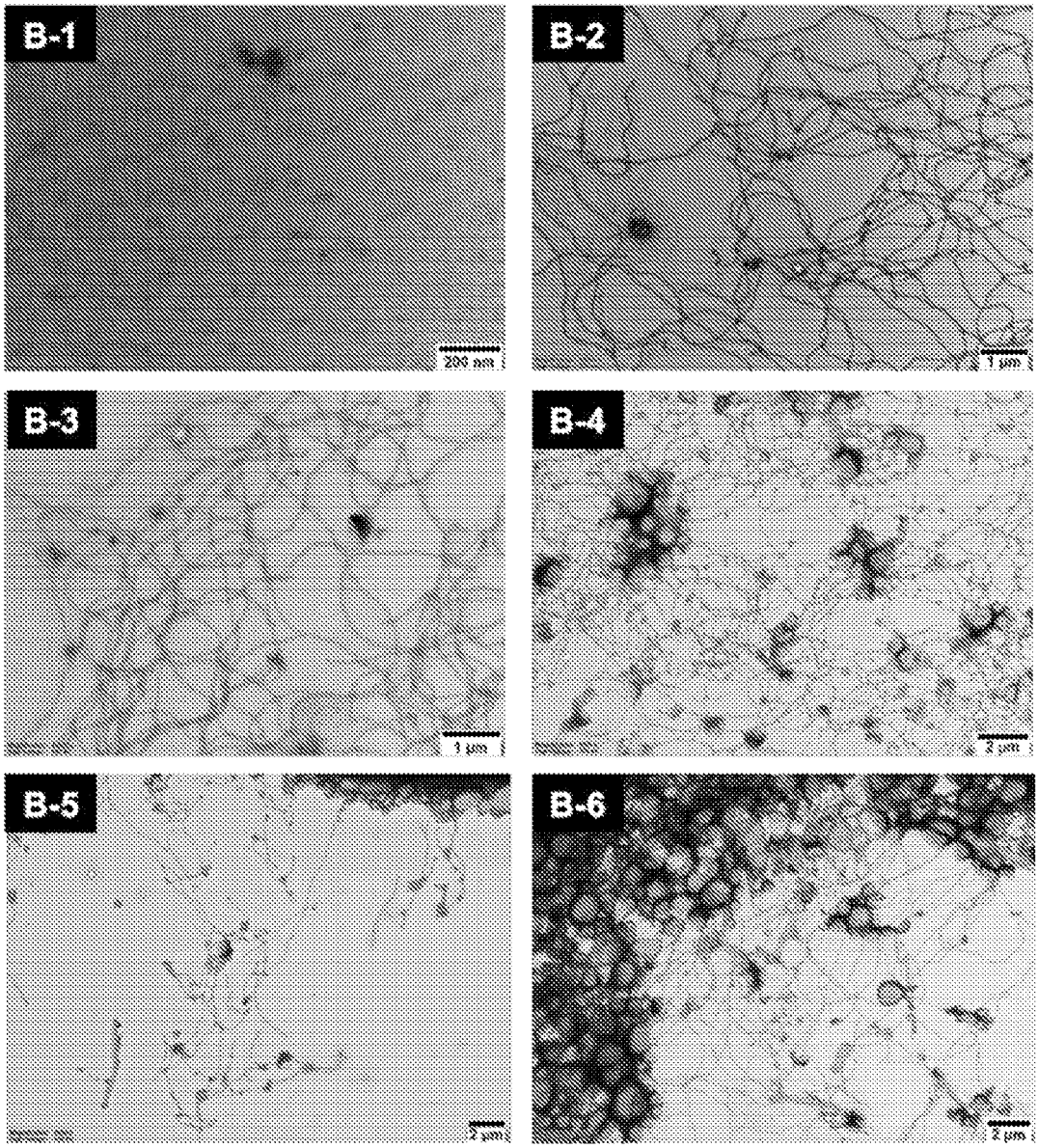


Figure 5

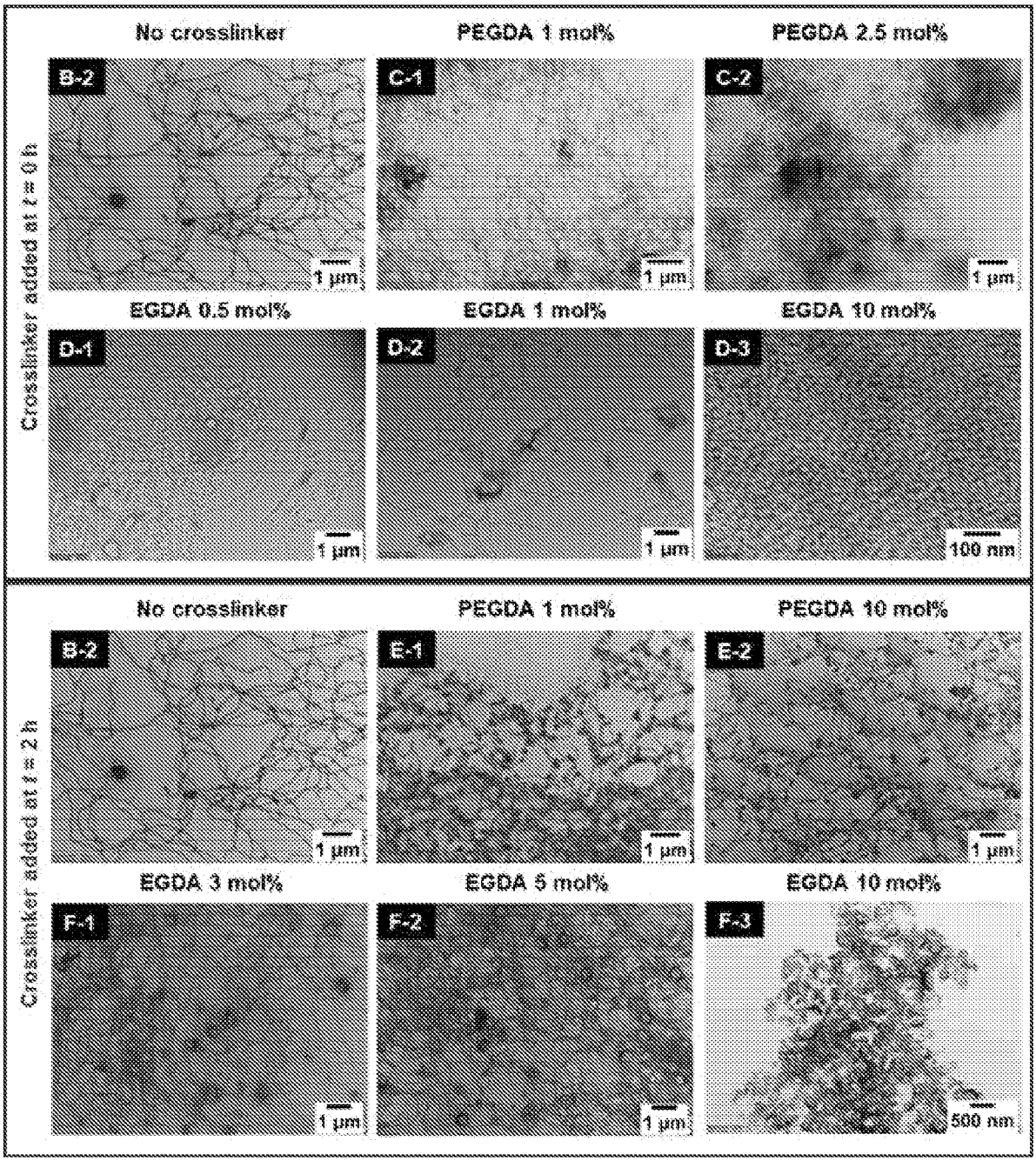

Crosslinker added at t = 0 h
No crosslinker
PEGDA 1 mol%
PEGDA 2.5 mol%
B-2
C-1
C-2
1 µm
EGDA 0.5 mol%
EGDA 1 mol%
EGDA 10 mol%
D-1
D-2
D-3
1 µm
100 nm
Crosslinker added at t = 2 h
No crosslinker
PEGDA 1 mol%
PEGDA 10 mol%
B-2
E-1
E-2
1 µm
EGDA 3 mol%
EGDA 5 mol%
EGDA 10 mol%
F-1
F-2
F-3
1 µm
500 nm

Figure 6

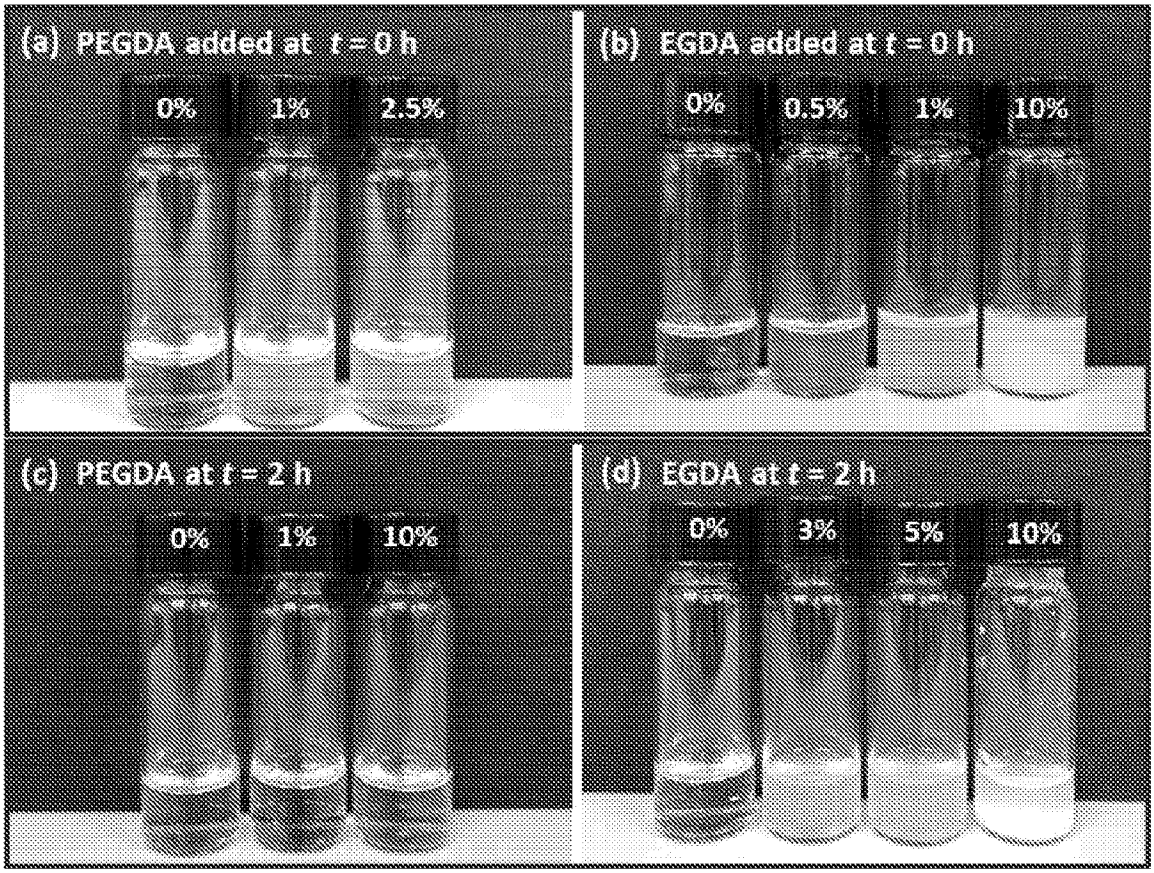

(a) PEGDA added at t = 0 h
0%
1%
2.5%
(b) EGDA added at t = 0 h
0%
0.5%
1%
10%
(c) PEGDA at t = 2 h
0%
1%
10%
(d) EGDA at t = 2 h
0%
3%
5%
10%

Figure 7

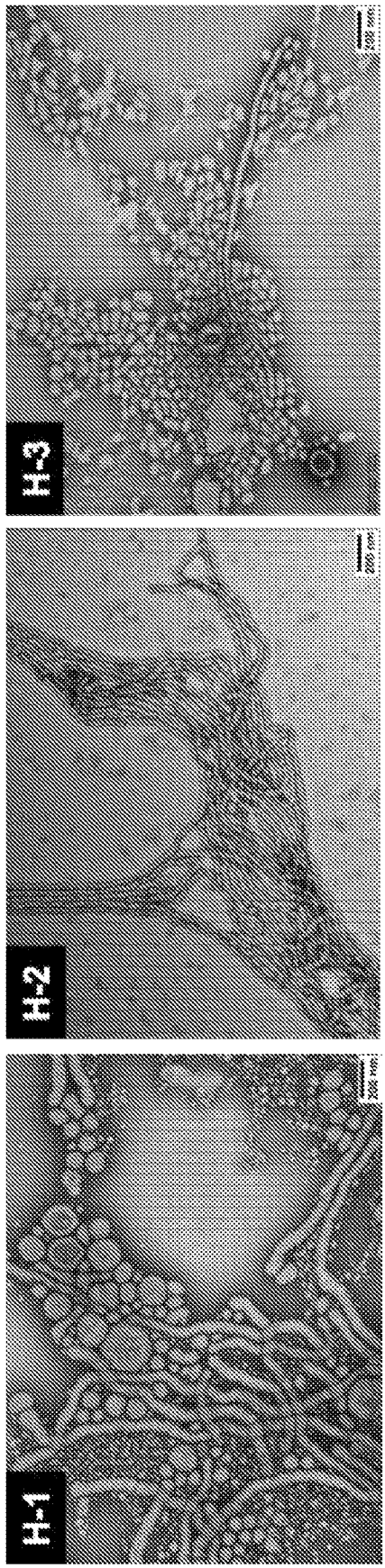


Figure 8

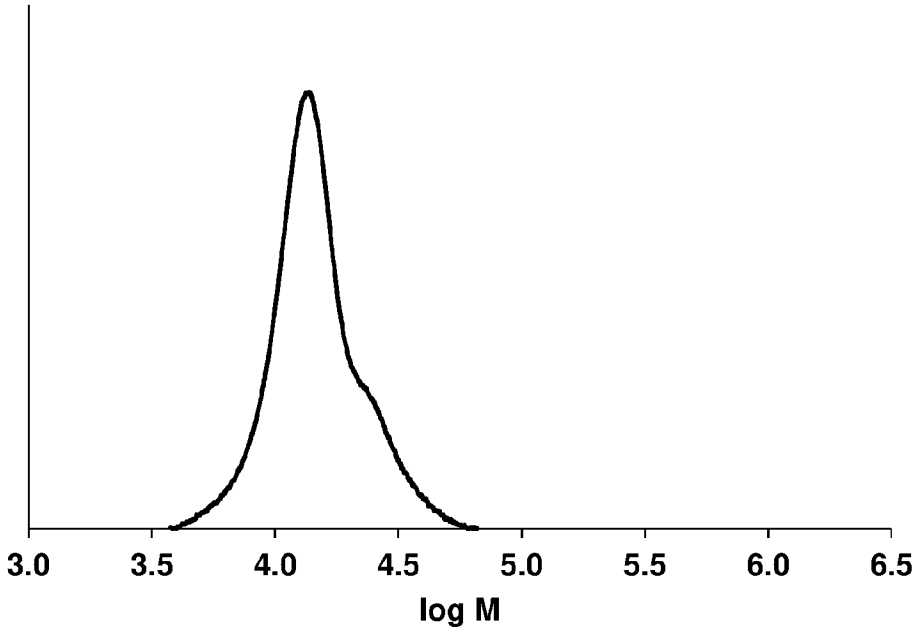


Figure 9

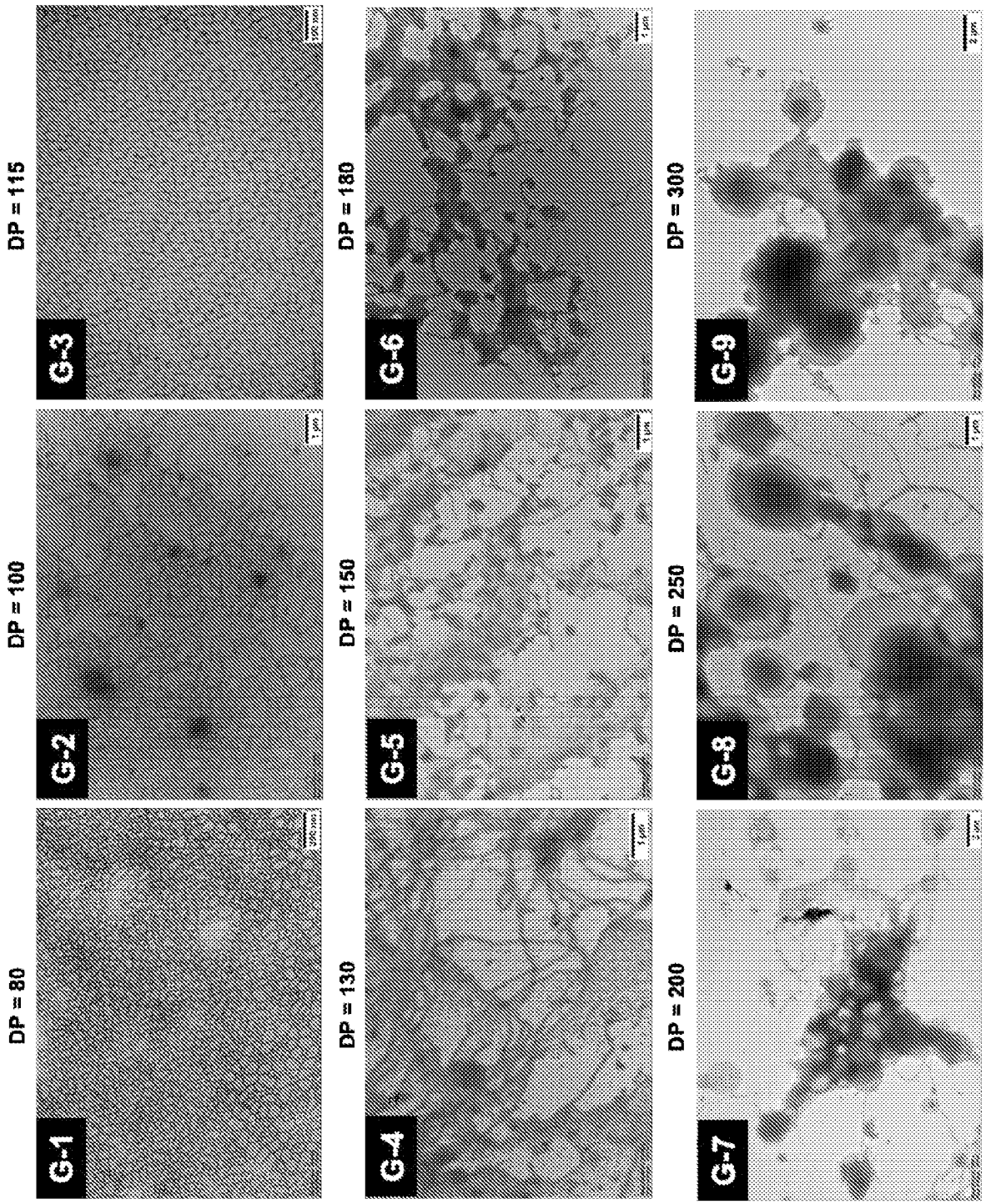

DP = 80
G-1
DP = 100
G-2
DP = 115
G-3
DP = 130
G-4
DP = 150
G-5
DP = 180
G-6
DP = 200
G-7
DP = 250
G-8
DP = 300
G-9

Figure 10

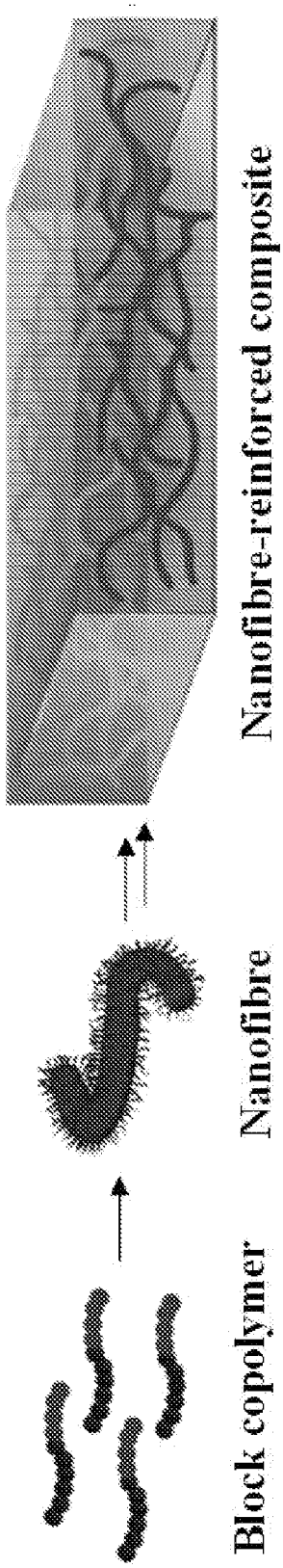

Nanofibre-reinforced composite
Nanofibre
Block copolymer

Figure 11

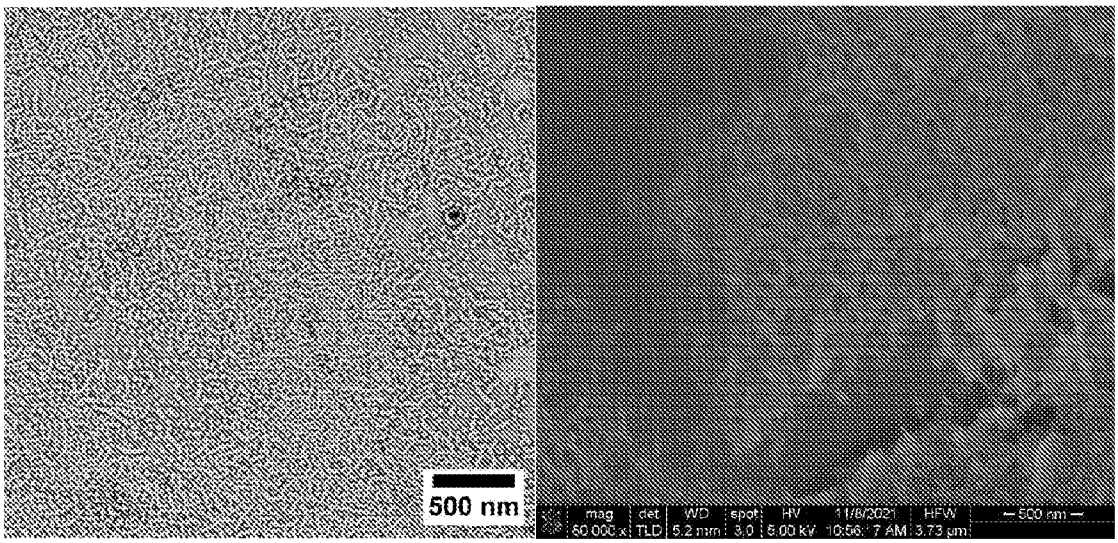

500 nm
mag det WD spot HV 11/8/2021 HFW 500 nm
50 000 x TLD 5.2 mm 3.0 5.00 kV 10:56:17 AM 3.73 µm

Figure 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2022/051458

A. CLASSIFICATION OF SUBJECT MATTER

D01F 8/10 (2006.01) B82Y 30/00 (2011.01) B82Y 40/00 (2011.01) C08F 212/08 (2006.01) C08F 220/18 (2006.01) C08F 265/06 (2006.01) C08F 287/00 (2006.01) C08F 293/00 (2006.01) C08J 5/00 (2006.01) C08J 5/18 (2006.01) C09D 7/40 (2018.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PATENW, CAPLUS, PQSCITECH, SCISEARCH, RAPRA, WPIX, GOOGLE SCHOLAR, ESPACENET (IPC and CPC Marks: C08F212/08, C08F220/1804, C08F220/1807, C08F220/1808, C08F2/22, C08F2/001, C08F2/16, C08F293/005, C08F287/00, C08F265/06, D01F8/10, B82Y40/00, B82Y30/00, C08J5/00, C08J5/18, C09D7/40, C09D7/70, C08F2438/03, C08J5/005, D10B2321/08, D10B2321/121; Keywords: Amphiphilic, Hydrophilic, Hydrophobic, Block copolymer, Fiber, Fibre, Worm, Core, Shell, Acrylic acid, Ethylene glycol methyl ether acrylate, ethylene glycol methyl ether methacrylate, PEGA, PEGMA, Styrene, Butyl acrylate, Methyl acrylate, Methyl methacrylate, Ethyl hexyl methacrylate, Benzyl methacrylate, PMMA, PBzMA, PEHMA RAFT, ATRP, NMP, RDRP, Film, Coat, Matrix, Binder, Composite, Viscosity, Rheology, Thickener and associated terms); ESPACENET : Applicant/Inventor Name Search : NEWSOUTH INNOVATIONS PTY LIMITED, UNSW, ZWITTERLUND PER B, ISHIZUKA FUMI, KIM HYUN JIN, CHATANI SHUNSUKE, NIINO HIROSHI; Applicant/Inventor name also searched in internal databases provided by IP Australia.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [ ] See patent family annex

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 2023	10 February 2023
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Balaji Rengarajan AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61 2 6285 0718

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2022/051458**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHANG, B. et al., "Morphological Stabilization of Block Copolymer Worms Using Asymmetric Cross-Linkers during Polymerization-Induced Self-Assembly", Macromolecules, 2018, Vol. 51, pages 2776−2784. See abstract; scheme 1; Figures 1-7; page 2777, column 2, last para-page 2781, column 2, para 1; supporting information	1-24
X	LOVETT, J. R. et al., "A Robust Cross-Linking Strategy for Block Copolymer Worms Prepared via Polymerization-Induced Self-Assembly", Macromolecules, 2016, Vol.49, pages 2928−2941. See abstract; page 2930, column 1, para 2-page 2939, column 1, first para; Figures 1-13	1-24
X	PHAM, B. T. T. et al., "Aqueous Polymeric Hollow Particles as an Opacifier by Emulsion Polymerization Using Macro-RAFT Amphiphiles", Langmuir, 2018, Vol. 34, pages 4255−4263. See abstract; page 4256. Column 2, para 3-page 4257, column 1, para 1; Figure 1, Table 1	1-24
X	CHENAL, M et al., "*Ab initio* RAFT emulsion polymerization of butyl acrylate mediated by poly(acrylic acid) trithiocarbonate", Polym. Chem., 2013, Vol. 4, pages 752-762. See abstract; page 753, column 2, para 4-page 754, column, last para; page 756, column 1, para 2-page 761, column 1, para 3; Figure 1; Tables 1-2	2, 4, 6-10 and 13
X	THOMPSON, K. I. et al., "Preparation of Pickering Double Emulsions Using Block Copolymer Worms", Langmuir 2015, Vol. 31, pages 4137−4144. See abstract; page 4138, column 2, para 2-page 4139, column 1, para 4; page 4139, column 1, last para- column 2, first para; page 4139, column 2, last para-page 4143, column 1, first para; Figures 1-3; Table 1	24-39
X	FIELDING, L. A. et al., "Thermo-responsive Diblock Copolymer Worm Gels in Non-polar Solvents", J. Am. Chem. Soc., 2014, Vol. 136, pages 5790−5798. See abstract; Figures 1-3, 5, 8, Table 1; page 5791, column 1, last para-5794, column 1, para 2; supporting information	25-39
X	THOMPSON, K.L. et al., "Vermicious thermo-responsive Pickering emulsifiers", Chem. Sci., 2015, Vol. 6, pages 4207-4214. See abstract; page 4208; column 2, para 2- page 4209, column 1, para4; page 4209, column 2, para 2-page 4213, column 2, first para; Figures 1-3; Table 1; supporting information	25-39

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2022/051458

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box

Continuation of: **Box III**

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-24 are directed towards (i) a polymeric nanofiber and its uses wherein the polymeric nanofiber having core-sell morphology wherein the shell is hydrophilic, and the core comprises: a) a hydrophobic copolymer, or b) a hydrophobic homopolymer; and (ii) an amphiphilic block copolymer comprising: a block [A] comprising a hydrophilic homo- or copolymer; and a block [B] comprising: a) a hydrophobic copolymer or b) a hydrophobic homopolymer. The feature of a polymer having a hydrophilic block and a hydrophobic block is specific to this group of claims.

- Claims 25-39 are directed towards (i) a block copolymer comprising: a hydrophobic block [A], wherein block [A] is substantially soluble in an 20/80 vol.% water/ethanol mixture; and a hydrophobic block [B] comprising at least one hydrophobic monomer, wherein block [B] is more hydrophobic than block [A] and is a different composition to block [A]; (ii) a method of producing said block copolymer; and (iii) a polymeric nanofiber and its uses wherein the polymeric nanofiber having a core-shell morphology, wherein the shell is hydrophobic, and the shell comprises a polymer that is substantially soluble in an 20/80 vol.% water / ethanol mixture; and wherein the core is hydrophobic, and the core comprises a polymer that is more hydrophobic than the polymer of the shell, and is a different composition to the polymer of the shell. The feature of a polymer having two hydrophobic blocks is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is "a polymer having a hydrophobic block".

However this feature does not make a contribution over the prior art because it is disclosed in:

each of D1-D7.

Therefore in the light of this document this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.