

**Title:** GRAFT BLOCK COPOLYMER SURFACTANT AND METHODS TO DO THE SAME

**Abstract:** A graft block copolymer surfactant has a backbone comprising a backbone moiety, hydrophilic blocks and hydrophobic blocks. The hydrophilic blocks have a molecular weight of at least 319 Daltons, the hydrophobic blocks have a molecular weight of at least 300 Daltons and the surfactant has an overall molecular weight in the range 3000 to 70000 Daltons. Also disclosed are methods of making the surfactant; compositions made using the surfactant and a method of breaking an emulsion made using the surfactant.
The present invention relates to surfactants; particularly graft block copolymer surfactants, and compositions containing them. The surfactants of the present invention are particularly suitable for use in industrial fluids. The present invention also relates to methods of producing such surfactants.

GB2002400A and GB2117398A each describe certain graft copolymers and methods of their production. In particular, these graft block polymers are prepared by reacting a poly(hydroxy carboxylic acid) having a terminal carboxylic group with a polyalkylene glycol or a polyether polyol, respectively. The graft block copolymers can be used as wetting and dispersing agents, as emulsifiers, as emulsion stabilisers and in compositions for use in cutting oils and other metal working fluids and fluids for hydraulic power transmission. One disadvantage of these prior art industrial fluids is that they may be prone to inversion during e.g. a spraying process. Inversion occurs when the oil-in-water emulsion inverts to a water-in-oil emulsion as a result of the mechanical stress of very high pressure spraying. Typically the inversion event is short lived, but it may still be significant. The problematic effects of such inversions are two-fold - lubricating properties are lost in the inverted solution, and deposits of viscous hydrophobic components accumulate on the spray nozzle. The deposits of inverted solution at areas of high shear build up over time and eventually the residue will enter the system as a high oil content "slug". The second effect is potentially more of a problem as such a slug of oil rich residue seriously contaminates the metal surface.

US 5.536.445 to Zeneca Ltd. discloses block polymers that are for example prepared by first reacting a poly(hydroxy carboxylic acid) with a
linking compound such as polyols, e.g. glycerol, polyamines, e.g. hexamethylene diamine and hydroxyamines, e.g. dipropanol amine, and subsequently with a compound having an acid group, e.g. \(\alpha\)-amino carboxylic acid and aminoethane sulphonic acid. These block polymers are suitable as surfactants.

US 5.385.687 to Exxon discloses polymeric ashless dispersants for lubricating oils. These polymeric ashless dispersants are prepared by reacting an intermediate product, said intermediate product obtained by condensation of a polyanhydride, e.g. a dianhydride, and a polyamine, a polyl or an amino alcohol, with a long chain hydrocarbyl dicarboxylic acid producing material, e.g. polyisobutenyl succinic anhydride.

US 5.482.519 to Exxon discloses similar polymeric ashless dispersants, wherein the intermediate product is obtained by condensation of a polyepoxide, e.g. a diepoxide, with a polyamine, e.g. tetramethylene pentamine.

US 5.756.428 to Exxon discloses high functionality, low molecular weight polymeric ashless dispersants for lubricating oils that are prepared by reacting a hydrocarbyl dicarboxylic acid producing material having 1.3 to 1.8 dicarboxylic acid producing moieties, e.g. a polyisobutenyl succinic anhydride having 1.53 succinic anhydride moieties per polyisobutene molecule, with a nucleophilic reactant such as polyamines, polyls, amino alcohols and mixtures thereof.

The present invention provides a novel graft block copolymer surfactant that provides a number of advantages over the prior art polymeric surfactants. Significantly, it is able to form an extremely stable emulsion that exhibits inversion stability. Furthermore the stable emulsion has the
ability to tolerate the presence of inorganic and organic particulates, for example metal powders, fines, ceramics, carbonaceous particulates and slurries, for example coal, and retain them largely within the body of the fluid.

According to a first aspect of the present invention there is provided a graft block copolymer surfactant having

- a backbone comprising a backbone moiety, hydrophobic blocks having a molecular weight of at least 319 daltons (Da), and hydrophilic blocks having a molecular weight of at least 300 Da,
- wherein the hydrophobic blocks project substantially in their entirety from the backbone to form grafts, and
- wherein the hydrophilic blocks form at least part of the backbone in conjunction with the backbone moiety or project substantially in their entirety from the backbone to form grafts, or a mixture of the two;
- wherein the graft block copolymer surfactant has a molecular weight of from 3000 to 70000 Da.

In a preferred embodiment the hydrophobic blocks project from the backbone to form grafts and the hydrophilic blocks are integral with the backbone.

Suitably the hydrophilic blocks comprise a hydrophilic polymer having a molecular weight of between 300 and 5,000 daltons (Da), preferably 400 to 1000 Da, which is soluble in water to the extent of at least 5% by weight at 25°C. It will be understood that there are a large number of potentially suitable hydrophilic blocks and block precursors which can be used in the present invention, and suitable hydrophilic blocks and hydrophilic block precursors will be apparent to the person skilled in the art. Suitable hydrophilic blocks are typically derived from polyvalent hydrophilic block
precursors, e.g. divalent or trivalent molecules, the polyvalency allowing the precursors to be combined into the block copolymer, either as part of the backbone or as a graft. Where a hydrophilic block is to be integral with the backbone, it is preferred that the block precursor is substantially linear and has active groups at opposite ends of the molecule. Where the hydrophilic block is to form a graft, it is preferred that the block precursor molecule comprises at least two active groups located relatively close together at one end of the precursor, e.g. on a polyvalent head portion. Suitably the hydrophilic blocks are derived from hydrophilic block precursor molecules which are polyols or polyamines, preferably diols or diamines.

In a particularly preferred embodiment the hydrophilic block is a polymer of a water soluble alkylene glycol. A preferred hydrophilic polymer is polyethylene glycol (PEG), preferably PEG having a molecular weight of 300 to 5,000 Da, more preferably 400 to 1000 Da, especially 400 to 800 Da. Alternatively, a mixed poly(ethylene-propylene glycol) or mixed poly(ethylene-butylene glycol) may be used provided they achieve the desired water solubility criteria. Exemplary hydrophilic blocks for use in the present invention may comprise PEG400, PEG600 and PEG1000. PEG has significant advantages over many other hydrophilic polymers as it burns very cleanly, thus facilitating disposal of the surfactant after it has been used. PEG is also relatively cheap. It is generally preferred that the hydrophilic block makes up from 20% to 50% by weight of the graft block copolymer surfactant, preferably 30% to 45% by weight.

Other suitable hydrophilic blocks may be derived from diols and diamines containing acidic groups, e.g. carboxylic acid groups, sulphonyl groups (e.g. sulphonyl styrenic groups), amine groups (e.g. tetraethylene...
pentamine (TEPA) or polyethylene imine (PEI)), or hydroxyl groups (e.g. sugar based mono- or co-polymers).

Suitably the hydrophobic block comprises a hydrophobic polymer.

Suitable hydrophobic polymers include polyolefins, polyacrylics, polystyrenyls and selfcondensed fatty acids (e.g. polyhydroxyacrylic acid, vinyl acetate or polypropylene acid). The hydrophobic block is typically derived from a hydrophobic block precursor having a polyvalent head, preferably a divalent head, especially a diacid head. The polyvalent head allows the hydrophobic block to be incorporated into the block copolymer with the hydrophobic polymer extending from the backbone as a graft.

In a particularly preferred embodiment the hydrophobic polymer is suitably a polymer of a mono-olefin, in particular the polymer of a mono-olefin having from 2 to 6 carbon atoms, such as ethylene, propylene, butene-1 and isobutene. Such a polymer may conveniently be provided by the residue of a polyalk(en)ylsuccinic anhydride block precursor. Preferably the hydrophobic block is derived from an alk(en)yl succinic anhydride of the formula:

\[
\begin{align*}
&\text{R} - \text{CH} - \text{CO} \\
&\text{CH}_2 - \text{CO}
\end{align*}
\]

wherein \( R \) is a saturated or unsaturated, preferably unsaturated, hydrocarbon substituent derived from a polymer of a mono-olefin, the said polymer containing a chain of from 15 to 500 carbon atoms. A particularly preferred hydrophobic block is derived from a polyisobutylene succinic anhydride (PIBSA) block precursor having a molecular weight in the range of 319 to 5000 Da, preferably 500 to 1500 Da. Polyisobutylene succinic anhydrides are commercially available compounds made by an addition
reaction between poly(isobutene) having a terminal unsaturated group and maleic anhydride.

The backbone moiety may be derived from essentially any polyvalent precursor molecule suitable to form bonds with the hydrophobic block precursors and/or hydrophilic block precursors via their respective reactive groups. Generally polyols, poly-carboxylic acids and polyamines form suitable backbone moieties. Polyols are particularly preferred backbone moieties. The polyol may be a diol, triol, tetrol and/or related dimers or trimers or chain extended polymers of such compounds. Examples of suitable polyols include glycerol, neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolebutane; pentaerythritol, dipentaerythritol, tripentaerythritol and sorbitol. In a preferred embodiment the polyol is glycerol. Glycerol has the advantage of being cheap and also burning cleanly.

It will be clear that the reactive groups of the backbone moiety precursor, the hydrophilic block precursor and the hydrophobic block precursor will be selected such that they are able to form bonds between them in the desired conformation. For example, the divalent succinic acid head of PIBSA is able to form an ester bond with hydroxyl group on the glycerol with one reactive group, and another ester bond with the hydroxyl group of PEG with the other reactive group.

The graft block copolymer of the present invention preferably comprises a plurality of linked copolymer subunits, each comprising at least one hydrophobic block, at least one hydrophilic block and a backbone moiety. The copolymer subunits are preferably identical such that they form repeating subunits in the graft block copolymer, though it is possible that each subunit may not be identical. The copolymer subunits may be joined
directly together or may, more preferably, be joined using a linker moiety, which generally will then form part of the backbone of the completed graft block copolymer surfactant.

Suitably the copolymer subunits are linked by a linker moiety. The linker moiety is typically derived from a molecule having at least two reactive groups, i.e. is divalent, and which is capable of linking two subunits together. The exact structure of the linker moiety is not generally significant, given that its function, like the backbone moiety, is simply to link two reactive groups on the copolymer subunits. The linker moiety is preferably derived from a substantially linear molecule with reactive groups at opposing ends, such that it is able to link to reactive groups on each of the copolymer subunits and minimise steric hindrance. The linker molecule is suitably a divalent hydrocarbon group, e.g. it may suitably be a saturated or unsaturated aliphatic hydrocarbon group, and is suitably derived from an aliphatic dibasic acid, preferably containing up to 20 carbon atoms, more preferably up to 12 carbon atoms. Suitably the linker moiety is derived from a polycarboxylic acid, for example a di- or tricarboxylic acid. Dicarboxylic acids are preferred linkers, particularly straight chained dicarboxylic acids, though branched chain dicarboxylic acids may also be suitable. Particularly suitable are straight chained dicarboxylic acids having a chain length of between 2 and 10 carboxylic acids, for example oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic or sebacic acid. Unsaturated dicarboxylic acids such as maleic acid may also be suitable. A particularly preferred linker molecule is adipic acid, which is both cheap and clean burning. Alternative linker molecules are low molecular weight alkenyl succinic anhydrides (ASA), such as \( \text{C}_{18} \) ASA.
Generally the copolymer subunit comprises two or more hydrophobic blocks, two or more hydrophilic blocks and a backbone moiety. In a preferred embodiment the copolymer subunit comprises two hydrophobic blocks being present as grafts and two hydrophilic blocks, the hydrophilic blocks being integral with the backbone, the copolymer subunit comprising a further backbone moiety. In such an embodiment each hydrophobic block may conveniently comprise a divalent head portion, one valent group of said head portion of each hydrophobic block being linked to different, preferably opposing, points on the backbone moiety, the other valent group of said head portion of each hydrophobic block being linked to one or other of the hydrophilic blocks. Thus a subunit structure is provided in which a central backbone moiety is flanked by two hydrophobic blocks which, in turn, are attached to two hydrophilic blocks. These copolymer subunits are linked together to form the graft block copolymer. These copolymer subunits may be linked directly, i.e. via the hydrophilic block on one subunit to a corresponding hydrophilic block on another subunit, or may be linked via a linker molecule between the two hydrophilic blocks as mentioned above.

By the terms hydrophobic block precursor, hydrophilic block precursor, backbone moiety precursor, and linker moiety precursor it is meant precursor molecules which are reacted together, via reactive groups present on the precursor molecules to form the respective moiety or block in the copolymer. Thus the moiety or block is derived from a precursor which is combined into the block copolymer, e.g. by condensation.

In one embodiment the present invention provides a graft block copolymer surfactant comprising a repeating copolymer subunit having the general structure:

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Hydrophile     Backbone     Hydrophile
      |              |              |
      v              v              v
Hydrophobe     Hydrophobe     Hydrophobe
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The graft block copolymer surfactant typically comprises from 2 to 20 copolymer subunits, preferably from 3 to 15 subunits, more preferably 3 to 10 subunits, especially 3 to 7 subunits. The number of subunits can be selected to achieve the desired property of the surfactant, in particular the viscosity.

In a particularly preferred embodiment of the present invention the repeating copolymer subunit has the following structure:

- The links between the subunits are shown as lines. This is because the nature of the link is not generally significant to the graft block copolymer surfactant. The person skilled in the art would select constituents with suitable reactive groups to allow the combination of subunits into the desired structure. Such design is routine on the field of polymer design.

- In general the links may be obtained via simple condensation reactions, e.g. between PIBSA and the polyol, between PIBSA and PEG and between PEG and a linker molecule, e.g. adipic acid. In the schematic structure given above the link between the glycerol and PEG is achieved via the diacid head of PIBSA, and this forms a preferred means of linking the precursor of the present invention.

- The present invention, in one aspect, may thus comprises a graft block copolymer surfactant comprising general structure:
wherein A is the copolymer subunit described above and R represents a unit terminating the backbone of the copolymer. As mentioned above n is suitably an integer from 1 to 19, preferably from 2 to 14, especially 2 to 6.

R may be essentially any moiety as its effects on the entire copolymer structure are generally insignificant. R may, in some embodiments, simply be the terminal group of the hydrophilic group. Where the hydrophilic block is PEG, R may conveniently be a hydroxyl group. However, particularly when the subunit A ends in a reactive group (e.g. as with the OH in PEG), it may be desirable or useful in many circumstances to introduce a chain terminating group to the end of the copolymer subunit. In this case the moiety R is typically formed by the addition of a monovalent hydrocarbon or substituted hydrocarbon group. It is, for example, particularly simple to attach a carboxylic acid to an exposed hydroxyl group on PEG via an ester linkage. In this respect any fatty carboxylic acid would be suitable. Suitable fatty acids include palmitic acid, oleic acid and linoleic acid. A particularly preferred fatty acid for combination with the surfactant is tall oil fatty acid (TOFA), a derivative of tall oil, which is primarily oleic acid.

The graft block copolymer surfactant of the present invention has a molecular weight of from 3,000 to 70,000 Da, preferably from 8,000 to 55,000 Da, more preferably from 8,000 to 40,000 Da especially from 8,000 to 25,000 Da. Generally a composition comprising the graft block copolymer surfactant of the present invention will comprise a range of copolymer chains of different lengths such that there will be a range of molecular masses in a particular composition. In such a case it is desirable that a substantial portion of the surfactant molecules are within the abovementioned size ranges. The surfactant may suitably have a number average molecular weight ($M_n$) of from 1000 to 4000, preferably
1200 to 3500, especially 1500 to 3000. A suitable weight average molecular weight ($M_w$) for the surfactant is from 6,000 to 70,000, preferably 9,000 to 50,000, especially 9,000 to 24,000.

The graft block copolymer surfactant of the present invention provides a number of advantages over the prior art. Significantly, it is able to form extremely stable emulsions, in particular emulsions stable against inversion. This property is believed to be a result of the large size of the surfactant molecule, such that the surfactant can essentially cover significant areas of droplets of oil in the emulsion; the hydrophobic "teeth" extending into the oil droplet, while the hydrophilic backbone forms a layer, akin a membrane, parallel to the surface of the droplet. Such a structure would be expected to be highly stable and would thus stabilise the emulsion much more than a smaller, e.g. monomeric, surfactant.

Furthermore the stable emulsion has the ability to tolerate the presence of inorganic and organic particulates, for example metal powders, fines, ceramics, carbonaceous particulates and slurries, for example coal, and retain them largely within the body of the fluid.

The graft block copolymer of the present invention is particularly suitable for use in industrial fluids. Such industrial fluids include hydraulic, in particular fire resistant hydraulic fluids, quenching fluids, chain oils and fluids for use in metal passivation.

In a further aspect the present invention provides a method of producing a surfactant, the method comprising the steps of:

- providing a hydrophobic block precursor;
- providing a backbone moiety precursor;
- providing a hydrophilic block precursor;
- providing a linker moiety precursor;
- reacting the hydrophobic block precursor, backbone moiety precursor, and hydrophilic block precursor to from a copolymer subunit; and
- reacting the copolymer subunit and the linker moiety precursor to form a graft block copolymer surfactant.

The method may optionally comprise the additional steps of:
- providing a chain terminating agent; and
- reacting the graft block copolymer with the chain terminating agent.

The reaction may conveniently be performed in two or more distinct reaction steps, wherein in subsequent steps materials are added to the reaction. A first step may involve a reaction to form a copolymer subunit, which is suitably continued until a desired amount of copolymer subunit is produced. In a second step the linker moiety precursor may be added and the reaction continued to allow the linker moiety to link copolymer subunits together. The second reaction is continued until the desired amount of graft block copolymer surfactant is formed.

The formation of the copolymer subunit may itself involve more than one step. For example, the reaction may involve the formation of an intermediate subunit comprising the hydrophobic block and the backbone moiety, to which the hydrophilic block is then added. There are, of course, other ways in which the copolymer subunit may be built up, and the best route to a particular subunit would be determined by the person skilled in the art as a matter of routine.

Accordingly, in one embodiment, the method of producing a surfactant, may comprise the steps of:

- providing a hydrophobic block precursor;
- providing a backbone moiety precursor;
- reacting the hydrophobic block precursor and backbone moiety precursor to from a reaction product;
- providing a hydrophilic block precursor;
- reacting the hydrophilic block precursor and reaction product to from a copolymer subunit;
- providing a linker moiety precursor; and
- reacting the copolymer subunit and the linker moiety precursor to form a graft block copolymer surfactant.

The method may optionally comprise the additional steps of:
- providing a chain terminating agent; and
- reacting the graft block copolymer with the chain terminating agent.

However, on the other hand, the reaction may be performed in a single step or single batch, i.e. without the addition of a further reagent after the reaction has been initiated. In such a method the hydrophobic block precursor, backbone moiety precursor, hydrophilic block precursor and linker moiety precursor are all provided at the start of the reaction. The reaction may then be progressed under conditions which favour the formation of the copolymer subunit until a desired amount of polymer subunit is formed. The reaction may then be progressed under conditions which favour the linking of copolymer subunits to form the graft block copolymer surfactant. Such a system is dependent on the copolymer subunit formation and the linking of the copolymer unit reactions being favoured at different reaction conditions. It is, however, within the skill of the person skilled in the art to determine suitable constituent parts to achieve such preferential reactions. In many systems a change of reaction temperature and/or pressure may be suitable to achieve the desired conditions to favour the particular reaction. Alternatively, other
conditions such as pH, presence/absence of a catalyst, or concentration of reactants could be used to modulate the reaction as required.

Accordingly, in one embodiment, the method of producing a surfactant, may comprise the steps of:

- providing a hydrophobic block precursor;
- providing a backbone moiety precursor;
- providing a hydrophilic block precursor;
- providing a linker moiety precursor; and

- reacting the hydrophobic block precursor, the backbone moiety precursor, the hydrophilic block precursor and the linker moiety precursor to form a graft block copolymer surfactant.

Various preferred precursors are detailed above, and these may be used in the method of the present invention.

Particularly preferred precursors are that the hydrophobic block precursor is PIBSA, the backbone moiety is a glycerol, the hydrophilic block precursor is PEG, especially PEG₆₀₀ and the linker moiety precursor is adipic acid.

One example of suitable conditions for a single step or single batch reaction involves addition of the hydrophobic block precursor, backbone moiety precursor, hydrophilic block precursor and linker moiety precursor into a single pot and reaction at a temperature of between 160 to 240°C, preferably 190 to 220°C until an acid value of less than 10, preferably less than 7, especially less than 3 is achieved for the product graft copolymer surfactant.
Of course, reaction conditions may be changed between steps where a multi-step reaction is used, and in most cases would be to optimise reaction rate and efficiency, though in this case it may not be as critical to formation of the end product.

In a preferred embodiment the method may comprise the following steps:
- a hydrophobic block precursor and a backbone moiety precursor are reacted in a suitable reactor under suitable conditions to form a first reaction product;
- a hydrophilic block precursor is then added to the reaction mixture;
- the hydrophilic block precursor and the first reaction product are reacted under suitable conditions to form a copolymer subunit; and
- a linker moiety precursor is then added to the reaction mixture and reacted under suitable conditions to form the graft block copolymer surfactant.

Various preferred precursors are detailed above, and these may be used in the method of the present invention.

In a particularly preferred embodiment the method may comprise the following steps:
- PIBSA and a glycerol are reacted in a suitable reactor under suitable conditions to form a first reaction product;
- PEG is then added to the reaction mixture;
- PEG and the first reaction product are reacted under suitable conditions to form a copolymer subunit; and
- adipic acid is then added to the reaction mixture and reacted under suitable conditions to form the graft block copolymer surfactant.

It is preferred that PEG_{600} is used in the method.
Suitably the PIBSA and glycerol are reacted at from 70 to 140°C, preferably approximately 120°C. Typically a reaction time of 2 hours or more is suitable to obtain a desired level of reaction product, preferably 3 hours or more, especially until greater than 90% of the anhydride has been converted. This is indicated by monitoring the height of the 1860-1810 cm\(^{-1}\) and 1790-1750 cm\(^{-1}\) peaks in the infra red corresponding to anhydride functionality.

Suitably the first reaction product and the PEG are reacted at from 180 to 250°C, preferably 190 to 230°C, especially 200 to 225°C. Optionally titanium (IV) butanate (TnBT) catalyst may be added to catalyse conversion of the first reaction product to the copolymer subunit, i.e. following addition of the PEG\(_{600}\). Preferably the TnBT catalyst is not added until the reaction mixture is above 150°C, preferably 160°C or higher.

Suitably the adipic acid is reacted with the copolymer subunit at from 180 to 250°C, preferably 190 to 220°C.

Suitably the reaction is performed at atmospheric pressure under a blanket of a suitably inert gas, e.g. nitrogen.

The method may involve the step of adding a chain terminating agent, e.g. a fatty acid, and continuing the reaction to link the chain terminating acid to the block copolymer surfactant.

The method may involve the additional step of adding a solvent to the graft block copolymer surfactant to reduce the viscosity of the composition.
The graft block copolymer surfactant has a desired acid value of less than 10, preferably less than 7, more preferably less than 5 and especially less than 3.

In a further aspect the present invention provides a water soluble composition comprising the graft block copolymer surfactant as set out above. The graft block copolymer surfactant in the composition acts as an emulsifier, maintaining a hydrophobic lubricating agent in emulsion within the aqueous phase when added to water, e.g. as an oil-in-water emulsion.

The graft block copolymer surfactant may suitably comprise from about 0.1 to 6% by weight of the composition, more preferably from about 0.5 to 3% by weight of the composition, especially from about 1 to 2% by weight of the composition. Typically concentrations of 3% or less by weight are desirable.

In a further embodiment the invention provides an aqueous composition comprising from 1 to 10% of the abovementioned water soluble composition dispersed in water.

In a further embodiment the composition may be a mixture of the graft block copolymer surfactant and a solvent. The graft block copolymer surfactant of the present invention typically has very high viscosity, i.e. tar-like in consistency. In order to make the surfactant more amenable to packaging and use by the end user it is desirable to provide it in a pourable form. This may be achieved by the addition of a suitable solvent to produce a mixture of lower viscosity. Suitable solvents will be apparent to the person skilled in the art. Exemplary solvents include simple esters and simple lipophiles, which may be present at from 5 to 50% by weight, preferably 10 to 40%, especially 20 to 35%. Suitable esters are available.
from Croda under the trade name Priolube. Suitable lipophiles include dodecane.

In a further aspect the present invention provides a method of breaking an aqueous emulsion comprising the graft block copolymer surfactant and an oil component, the method comprising adding a polymeric cationic flocculating agent to the emulsion.

A preferred method of breaking an aqueous emulsion comprising the graft block copolymer surfactant and an oil component is to add a 0.5% solution of polymeric cationic flocculating agent to the emulsion until a concentration of 50 ppm is achieved in the emulsion, mix the emulsion then increase the pH to 7.

Magnafluc LT 22S is an example of a polymeric cationic flocculating agent.

Embodiments of the present invention will now be described, by way of example only.

Example 1 - Manufacture of a graft block copolymer surfactant

The following method is suitable for the formation of a graft block copolymer surfactant according to the present invention. The method detailed is suitable for production in a 200 Kg batch reactor, but the method is amenable to scale up.
The PIBSA and PEG are preheated to 50°C.

A clean and dry reactor is set to heat to 50°C.

The PIBSA is charged and a nitrogen blanket is applied.

The glycerol is then added and the temperature increased to 120°C.

The temperature is held for 4 hours.

The mixture is analysed by infra-red (IR) to determine if the reaction has reached the desired end point. The end point is indicated by the disappearance of anhydride peaks which are at 1860-1810 cm⁻¹ and 1790-1750 cm⁻¹.

If the specification is not reached then the reaction is continued for 2 hours and reassessed. This is continued until the desired specification is reached (e.g. the anhydride peak disappears) or there is no further reduction in the anhydride peak.

The PEG is then added to the reactor and the temperature increased to 220°C.

When the reactor temperature is over 150°C the TnBT is added.

The temperature is held for 4 hours.

The mixture is analysed to assess the acid number determine if the reaction has reached the desired end point. The acid number is ideally
as low as possible, with a value of 3.0 mg KOH/g being the upper limit in this example.

- If the specification is not reached then the reaction is continued for 1 hour and reassessed. This is continued until the desired specification is reached.

- The reactor is then cooled to 120°C and the adipic acid charged.

- The reactor is then heated to 220°C. If required the catalyst may be replaced.

- The temperature is held for 5 hours.

- The mixture is analysed to assess the acid number to determine if the reaction has reached the desired end point. A suitable end point is indicated by an acid value of 3 or less.

- If the specification is not reached then the reaction is continued for 1 hour and reassessed. This is continued until the desired specification is reached.

- Once the specification is reached the reaction is complete. The product of the reaction is an extremely viscous, tar-like liquid.

- The temperature is then reduced to 120°C, and a suitable ester is introduced to reduce the viscosity of the composition for easier storage or movement, e.g. barrelling. Suitable esters are marketed under the trade name Priolube, available from Croda.

Analysis of the product of the reaction reveals that the composition contains a mixture of polymer molecules of different sizes, with a $M_w$ of around 15,000 Da and a $M_n$ of around 2500. The material was particularly effective in forming stable emulsions.
Claims

1. A graft block copolymer surfactant comprising
   a backbone comprising a backbone moiety, hydrophobic blocks having a molecular weight of at least 319 daltons (Da), and hydrophilic blocks having a molecular weight of at least 300 Da,
   wherein the hydrophobic blocks project substantially in their entirety from the backbone to form grafts, and
   wherein the hydrophilic blocks form at least part of the backbone in conjunction with the backbone moiety or project substantially in their entirety from the backbone to form grafts, or a mixture of the two;
   wherein the graft block copolymer surfactant has a molecular weight of from 3000 to 70000 Da.

2. A graft block copolymer surfactant according to claim 1 comprising a repeating copolymer subunit having the general structure:

   ![Hydrophilic Blocks](image1)

   and having from 2 to 20 copolymer subunits.

3. A graft block copolymer surfactant according to claim 2 wherein the repeating copolymer subunit has the following structure:

   ![Hydrophilic Blocks](image2)
4. A method of producing a surfactant, the method comprising the steps of:
   - providing a hydrophobic block precursor;
   - providing a backbone moiety precursor;
   - providing a hydrophilic block precursor;
   - providing a linker moiety precursor;
   - reacting the hydrophobic block precursor, backbone moiety precursor, and hydrophilic block precursor to from a copolymer subunit; and
   - reacting the copolymer subunit and the linker moiety precursor to form a graft block copolymer surfactant.

5. The method of claim 4 comprising the additional steps of:
   - providing a chain terminating agent; and
   - reacting the graft block copolymer with the chain terminating agent.

6. The method of claim 4 or 5 comprising the steps of:
   - providing a hydrophobic block precursor;
   - providing a backbone moiety precursor;
   - reacting the hydrophobic block precursor and backbone moiety precursor to from a reaction product;
   - providing a hydrophilic block precursor;
   - reacting the hydrophilic block precursor and reaction product to from a copolymer subunit;
   - providing a linker moiety precursor; and
   - reacting the copolymer subunit and the linker moiety precursor to form a graft block copolymer surfactant.

7. The method of any one of claims 4 to 6 comprising:
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- a hydrophobic block precursor and a backbone moiety precursor are reacted in a suitable reactor under suitable conditions to form a first reaction product;
- a hydrophilic block precursor is then added to the reaction mixture;
- the hydrophilic block precursor and the first reaction product are reacted under suitable conditions to form a copolymer subunit; and
- a linker moiety precursor is then added to the reaction mixture and reacted under suitable conditions to form the graft block copolymer surfactant.

8. The method of claim 7 comprising the following steps:
- PIBSA and a glycerol are reacted in a suitable reactor under suitable conditions to form a first reaction product;
- PEG is then added to the reaction mixture;
- PEG and the first reaction product are reacted under suitable conditions to form a copolymer subunit; and
- adipic acid is then added to the reaction mixture and reacted under suitable conditions to form the graft block copolymer surfactant.

9. A method of producing a surfactant, the method comprising the steps of:
- providing a hydrophobic block precursor;
- providing a backbone moiety precursor;
- providing a hydrophilic block precursor;
- providing a linker moiety precursor;
reacting the hydrophobic block precursor, backbone moiety precursor, hydrophilic block precursor and the linker moiety precursor to form a graft block copolymer surfactant.
10. A water soluble composition comprising the graft block copolymer surfactant of any one of claims 1 to 3.

11. An aqueous composition comprising from 1 to 10% of the water soluble composition of claim 10 dispersed in water.

12. A mixture of the graft block copolymer surfactant according to any one of claims 1 to 3 and a solvent.

13. A method of breaking an aqueous emulsion comprising the graft block copolymer surfactant according to any one of claims 1 to 3 and an oil component, the method comprising adding a polymeric cationic flocculating agent to the emulsion.
### INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C08G81/02 BO1F17/00

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)

C08G BO1F

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 practical, search terms used)

EPO-Internal, WPI Data, CHEMABS Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>X</td>
<td>GB 2 117 398 A (ICI PLC) 12 October 1983 (1983-10-12) cited in the application</td>
<td>1-13</td>
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<td>US 3 836 471 A (MILLER C) 17 September 1974 (1974-09-17) claim 12; example 8</td>
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Date of the actual completion of the International search

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