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Recent advances in the synthesis of polymeric surfactants

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Abstract

This article summarises the recent advances made in the synthesis of polymeric surfactants, particularly in the year 2000. One emerging theme is the increasing use of living radical polymerisation chemistry to prepare a wide range of new polymeric surfactants, which are expected to find use in many diverse areas. These include the preparation of new colloidal nanostructures, novel latex stabilisers and emulsifiers and various biomedical applications. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polymeric surfactants; Living radical polymerisation; Polymeric stabilisers; Emulsifiers; Block copolymer micelles; Colloidal nanostructures

1. Introduction

There is increasing interest in the synthesis of tailor-made polymeric surfactants. Although necessarily less well-defined than small-molecule surfactants, polymeric surfactants probably offer greater opportunities in terms of flexibility, diversity and functionality. This is especially true in the light of recent advances in controlled/living radical polymerisation chemistry, as exemplified by atom transfer radical polymerisation (ATRP) [1–7] and, to a lesser extent, reversible addition fragmentation transfer (RAFT) polymerisation [8]. This new polymer chemistry has enabled synthetic polymer chemists to make new, well-defined amphiphilic block copolymers, many of which exhibit interesting surfactant behaviour. In this review article we summarise the recent synthetic advances in the preparation of polymeric surfactants in the year 2000.

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2. Synthetic routes to polymeric surfactants

ATRP involves the use of an alkyl halide-based initiator in combination with a transition metal catalyst [usually Cu(I)] to polymerise vinyl monomers such as styrenics or (meth)acrylates [1–5]. The propagating intermediate is believed to be radical-based, thus this chemistry is particularly tolerant of functional monomers and can be performed in protic solvents, including water. Compared to conventional free radical polymerisation, the instantaneous radical concentration is believed to be relatively low due to rapid reversible de-activation (the polymer chains become capped with Br or Cl atoms), this means that termination reactions are suppressed relative to propagation. Thus, so-called 'pseudo-living' (co)polymers with relatively narrow molecular weight distributions are obtained ($Mw/Mn < 1.3$; in some cases, $Mw/Mn = 1.1$). RAFT chemistry is somewhat different in nature, but the same basic principle of rapid reversible deactivation applies, in this case by dithioesters [8]. One of the advantages of ATRP is that it is relatively easy to prepare macro-initiators, and hence functional block

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copolymer surfactants. One disadvantage is the relatively long reaction times and high temperatures usually employed in ATRP. However, Armes and co-workers have recently reported that the use of protic solvents such as water or lower alcohols can lead to much faster rates of polymerisation for ATRP even at 20°C [6]. This finding has now been confirmed by other workers [7] and augurs well for the synthesis of a wide range of novel, controlled-structure polymeric surfactants in the near future.

However, living polymerisation chemistry is by no means a pre-requisite for the synthesis of interesting new polymeric surfactants. Several groups have reported interesting examples based on classical free radical or step polymerisation chemistry (see below).

3. Amphiphilic diblock copolymers

The majority of work on polymeric surfactants concerns hydrophilic–hydrophobic diblock copolymers, where the hydrophobic block is permanently hydrophobic. Recently some attention has been given to hydrophilic–hydrophilic diblocks, in which the less hydrophilic block can be tuned to become hydrophobic by changing the external solution conditions, e.g. the solution pH, temperature or electrolyte concentration. In principle, this allows better control over the adsorption behaviour of these surfactants in aqueous media [9]. Recently, we have extended this approach to include so-called 'schizophrenic' AB diblock copolymers, which can form both micelles with the A block in the micelle core and also reverse micelles with the B block in the micelle core in aqueous solution (see Fig. 1). The original example reported [10,11•] was a tertiary amine methacrylate diblock copolymer prepared by group transfer polymerisation [GTP]; more recently we have discovered a second example based on poly[propylene oxide-*block*-2-(diethylamino)ethyl methacrylate] which is readily prepared by ATRP [12].

4. Other architectures

Sommerdijk et al. have described the remarkably rich phase behaviour of amphiphilic multi-block copolymers based on near-monodisperse poly(ethylene oxide) and polydisperse poly(methylphenylsilane) [13]. Spontaneous self-assembly in aqueous solution or THF/water mixtures led to a wide range of nanostructures, including vesicles, rod-like micelles, and helices. The polysilane block is s-conjugated and is hence sensitive to its conformational structure, which can be readily varied by manipulation of the solvent composition.

Following up their 1998 *Nature* paper, Scranton and co-workers [14] have published the full synthetic details of their statistical copolymerisation of methacrylic acid [MAA] and poly(ethylene glycol) methacrylate [PEGMA] by conventional free radical chemistry to produce high molecular weight, polydisperse emulsifiers whose surface activity is pH-dependent. At neutral pH the acidic residues are ionised and the copolymer behaves as a conventional polyelectrolyte, whereas at low pH the MAA residues are protonated and become intramolecularly hydrogen bonded to the ether oxygens on the adjacent PEG chains. This leads to the formation of alternating blocks of hydrophilic (uncomplexed) and hydrophobic (complexed) segments that stabilise oil-in-water emulsions in acidic media. This pH-dependent surface activity is completely reversible and could prove to be a convenient method for breaking emulsions.

Armentrout and McCormick have reported the synthesis of relatively high molecular weight polymeric surfactants by the statistical cyclocopolymerisation of a cationic and a sulfobetaine-based diallylic monomer [15]. At higher sulfobetaine contents, these copolymers form pH-reversible micro-domains which can sequester organic pollutants such as *p*-cresol. Applications in micellar-enhanced ultrafiltration processes for water purification are suggested.

Haddleton and co-workers briefly described the synthesis of unusual Y-shaped block copolymers in a recent review article [16]. A protected dihydroxy-func-

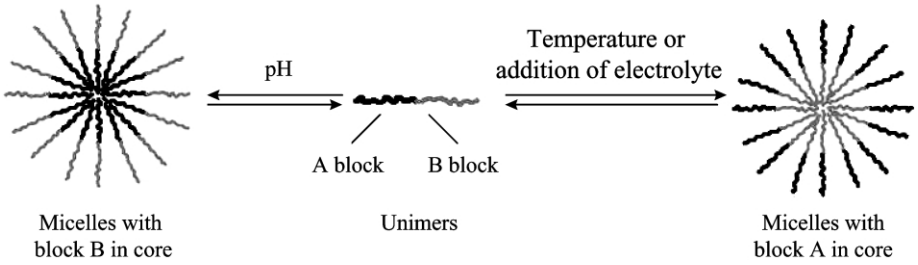


Fig. 1. Schizophrenic AB diblock copolymers based on 2-(diethylamino)ethyl methacrylate [DEA] can self-assemble to form either conventional micelles (block A in core) or reverse micelles (block B in core) at 20°C in aqueous media. Micellisation is induced by changing the solution pH, the electrolyte concentration or the solution temperature [10,11•,12].

tional initiator allows the controlled polymerisation of methyl methacrylate [MMA] by ATRP, then deprotection and esterification using 2-bromo-2-methyl propionyl bromide produced a trifunctional ATRP macro-initiator for the subsequent polymerisation of 2-(dimethylamino)ethyl methacrylate [DMA], a hydrophilic monomer. The final polydispersity was only 1.08, which suggests that the ATRP protocol [Cu(I)-based catalyst, *n*-alkyl pyridyl methanimine ligand, toluene, 90°C for 30 min) provided excellent control over the copolymer architecture. No aqueous solution properties were reported, but in view of packing constraints, these Y-shaped DMA-MMA polymeric surfactants might be expected to behave rather differently to their linear counter-parts in terms of both micellisation and interfacial activity.

5. Polymeric surfactants as latex stabilisers

Several groups have reported the use of novel polymeric surfactants in latex syntheses. For example, Antonietti and co-workers describe the synthesis of statistical comb copolymers comprising octadecyl side chains and carboxylic acid-based backbones via conventional free radical copolymerisation and their subsequent use of effective emulsifiers and steric stabilisers in the mini-emulsion polymerisation of styrene [17]. Burguiere et al. prepared two series of amphiphilic diblock copolymers using either ATRP or nitroxide-mediated polymerisation and investigated their efficacy as polymeric stabilisers in the emulsion polymerisation of styrene [18].

6. Siloxane-based polymeric surfactants

De Paz Banez et al. reported the synthesis of well-defined AB diblock copolymers where the A block comprised low molecular weight PDMS (Mn = 1100) and the B block comprised DMA residues. These copolymers formed micellar aggregates in water, as expected, but in some cases they can also self-assemble in solvents which are normally good solvents for the PDMS block [19]. Novel DMA-based surfactants were also prepared by the same group by the oxyanion-initiated polymerisation of DMA in THF using potassium *n*-alkyl alcoholate initiators [20].

A Texan group led by Johnston and Webber reported the preparation of so-called 'ambidextrous' ABC triblock copolymers via GTP by the sequential addition of first MMA and then trimethylsilyl methacrylate to a PDMS-based macro-initiator (see Fig. 2) [21•]. Removal of the silyl protecting groups produced hydrophilic MAA residues and this surfactant was successfully used for the preparation of PMMA latex in supercritical carbon dioxide ($scCO_2$). Here the PDMS chains act as the stabilising buoy block and both the neutral MMA block and the acidic MAA block are strongly adsorbed onto the latex surface since they are insoluble in $scCO_2$. Remarkably, on venting the CO_2, these latexes can be redispersed in water at up to 40% solids. Under these conditions the PDMS block becomes the non-solvated anchor block and the acidic MAA block becomes ionised in the aqueous phase, leading to efficient latex redispersion via a charge stabilisation mechanism.

A wide range of new PDMS-based diblocks have also been reported by Kickelbick and co-workers, who used anionic ring-opening polymerisation to block copolymerise the cyclic monomer hexamethylcyclotrisiloxane (D_3) with a methylvinylsiloxane [22]. Copolymer polydispersities were rather broad at 1.31–1.46, but the vinyl could be readily transformed via epoxidation into various hydrophilic groups, including primary amine, carboxylic acid, hydroxy and diol. Some cross-linking problems were encountered under certain conditions, and it remains to be seen whether these new PDMS-based diblocks have interesting surfactant behaviour.

Although there is much interest in $scCO_2$ as a

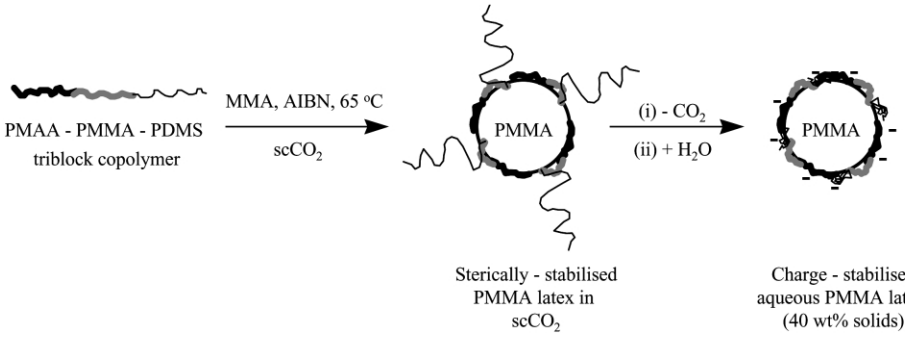


Fig. 2. PDMS-based 'ambidextrous' diblock surfactants are used to prepare sterically stabilised PMMA latexes in supercritical carbon dioxide [21•]. After venting the carbon dioxide, the same latexes can be redispersed in water at high solids, since ionisation of the surface carboxylic acid groups leads to charge stabilisation.

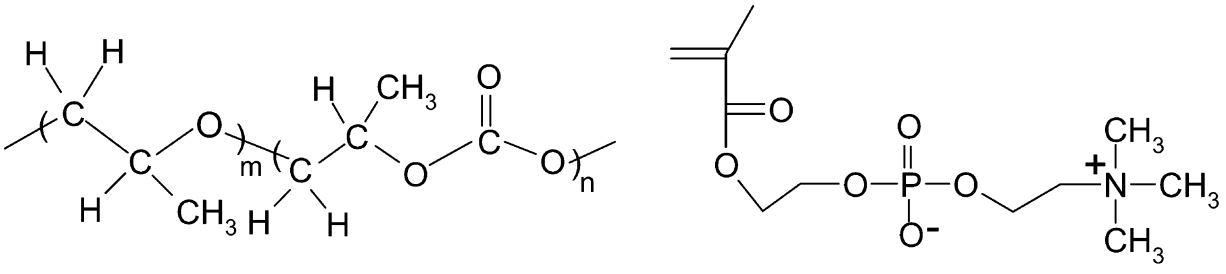
'green' solvent for polymer syntheses, one problem is that most polymers are insoluble in this solvent. This means that latex syntheses usually rely on the use of relatively expensive fluorinated or PDMS-based surfactants as steric stabilisers [23,24]. Howdle's group at Nottingham have described the derivatisation of commercially available maleic anhydride-based alternating copolymers with long-chain fluorinated alcohols [25]. These graft copolymers are effective stabilisers for the dispersion polymerisation of methyl methacrylate in $scCO_2$ and are probably marginally more cost-effective than the semi-fluorinated diblock copolymers reported previously. However, in a recent *Nature* paper, Beckman and co-workers reported that relatively inexpensive ether/carbonate-based alternating copolymers (see Fig. 3a) are remarkably soluble in $scCO_2$ [26•]. Since these copolymers can be designed to have terminal hydroxy functionality, the synthesis of ATRP macro-initiators and subsequent block copolymerisation with various (meth)acrylates should be straightforward. This is expected to provide access to a wide range of cost-effective hydrocarbon-based polymeric surfactants for $scCO_2$ syntheses in the near future.

7. Colloidal cross-linked nanostructures via polymeric surfactants

Growing attention has been given to the covalent stabilisation of self-assemblies of polymeric surfactants. Wooley's group have been pioneers in this area and they have begun to explore the potential of ATRP in this field [27]. Recently, they have reported the preparation of hollow 'nanocages' (see Fig. 4) based on cross-linked poly(acrylic acid) from parent shell cross-linked micelles by the selective hydrolytic degradation of the core-forming block, poly(e-caprolactone) [28•]. Similar hollow particles have also reported by Sakurai and co-workers [29]; in this case photochemical irradiation was used to remove the hydrophobic polysilane micelle cores and preliminary entrapment/release studies of the resulting poly(methacrylic acid)-based nanocapsules were undertaken using 5,6carboxyfluorescein as a fluorescence probe. Liu and co-workers have also made several important contributions in this field: for example, nanospheres with water-swollen cores were synthesised from hydrophilic–hydrophobic polymeric surfactants by: (1) micellar self-assembly in water/THF mixtures; (2) covalent stabilisation using 1,2-bis(2-iodoethoxy)ethane; (3) selective hydrolysis of the solketal methacrylate residues in the micelle core to produce hydrophilic glycerol-based moieties [30].

At Sussex we have recently shown that shell cross-linked micelle syntheses can be carried out successfully at high solids, provided that a suitable ABC triblock copolymer is used [31•]. ^{1}H NMR studies confirm that such triblock surfactants self-assemble in water to give three-layer 'onion' micelles, with the A block forming the solvated stabilising layer, the B block forming the inner shell and the C block forming the micelle core (see Fig. 5). Provided that the cross-linking chemistry is confined to the inner shell (the B block), covalent stabilisation can be achieved in concentrated solution (> 10% solids) with minimal inter-micelle cross-linking or gelation. This enables shell cross-linked micelles to be prepared under industrially relevant conditions for the first time. Indeed, in very recent unpublished work based on this approach, a one-pot synthesis of shell cross-linked micelles at high solids in water starting from monomers has been perfected in our laboratory [32].

Nardin et al. have recently published an elegant paper [33•] describing the spontaneous self-assembly of a novel, if somewhat polydisperse, ABA triblock copolymer in aqueous solution (see Fig. 6). The central hydrophobic B block was based on PDMS and the



(a) (b)

Fig. 3. (a) This alternating copolymer is based on propylene oxide and carbon dioxide repeat units and is the first purely hydrocarbon-based copolymer to exhibit high solubility in supercritical carbon dioxide [26•]. Thus, it is expected to replace the more expensive fluorous and siloxane-based copolymers currently used as surfactants in this environmentally-friendly solvent. (b) Chemical structure of a phosphorylcholine-based methacrylate monomer [MPC]. MPC-containing copolymers exhibit excellent biocompatibility [36]; ATRP now offers the possibility of synthesising well-defined MPC-based block copolymer surfactants [39].

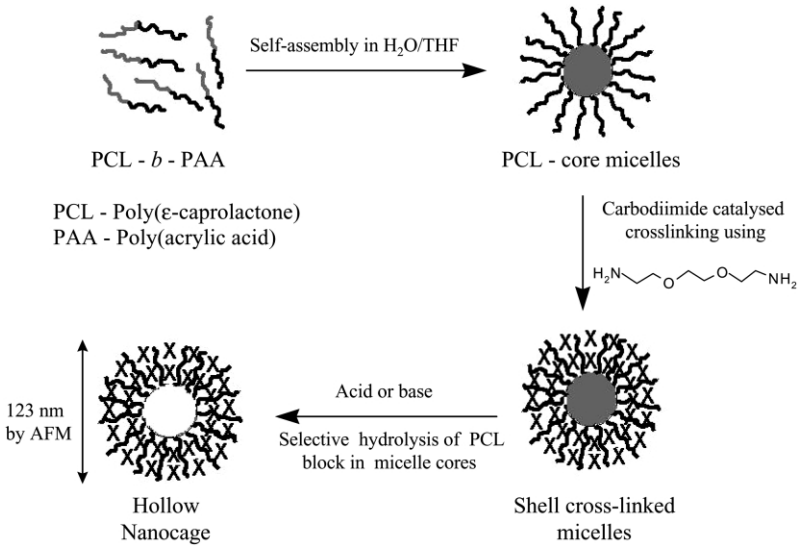
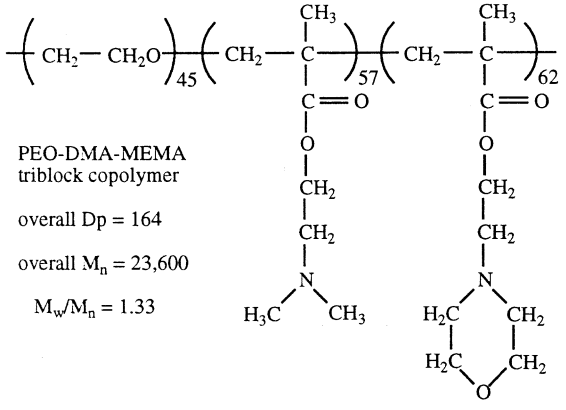


Fig. 4. Poly(e-caprolactone-*block*-acrylic acid) forms micelles in water/THF mixtures. Shell cross-linking is achieved via amidation chemistry; the amide linkages are much more stable towards hydrolysis than the polyester block in the micelle core. This allows removal of the poly(e-caprolactone) chains via selective hydrolysis to produce hollow 'nanocages' [28•].

two outer A blocks were poly(2-methyl oxazoline) [PMOXA]. The two terminal hydroxy groups were capped by reaction with 2-isocyanatoethyl methacrylate and, after self-assembly into polydisperse vesicles of 50–500 nm diameter and wall thickness of 10 nm, the resulting triblock copolymer chains could be



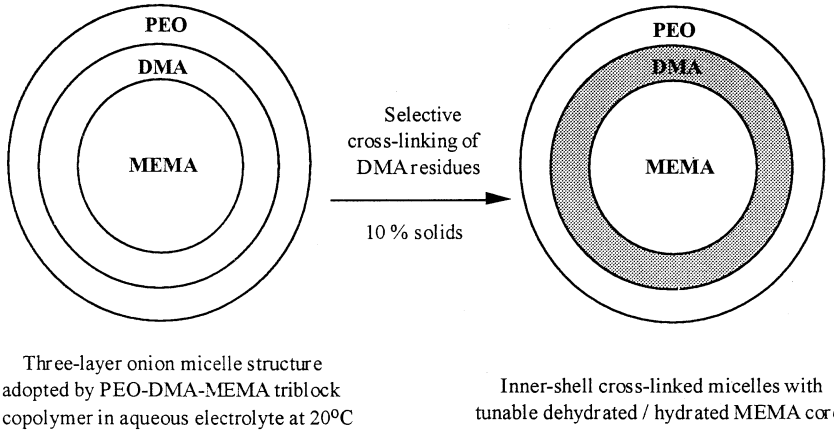


Fig. 5. Shell cross-linked micelles can be readily prepared in concentrated solution (> 10% solids) provided that an ABC triblock copolymer is used instead of the more conventional AB diblock copolymers [31•]. Cross-linking is confined to the tertiary amine-based DMA units in the inner shell; the outer shell of poly(ethylene oxide) acts as a steric stabiliser, thus preventing inter-micellar aggregation.

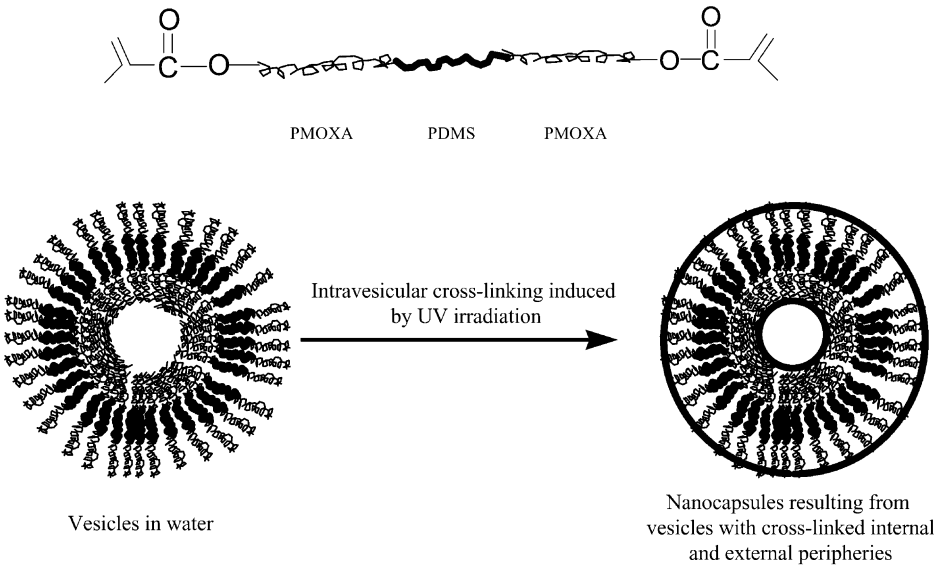


Fig. 6. An ABA triblock copolymer spontaneously self-assembles into polydisperse vesicles in aqueous solution at ambient temperature. Terminal methacrylate groups on each chain are oligomerised via UV irradiation to 'lock-in' the vesicular structure [33•].

cross-linked using UV irradiation. ^{1}H NMR indicated that more than 90% of the terminal vinyl groups had oligomerised, leading to covalent stabilisation of the internal and external peripheries of the vesicles. According to the authors, such vesicles show some promise as nanoreactors [34]. The same triblock copolymers can also be used to prepare giant free-standing membranes with geometric areas of 1 mm^2 and thicknesses of approximately 10 nm [35].

8. Biomedical applications

Since the early 1980s a phosphorylcholine methacrylate monomer (MPC; see Fig. 3b) has been used to formulate surface coatings for various biomedical applications [36]. The phosphorylcholine group is extremely hydrophilic and mimicks the chemical structure of cell membranes; cross-linkable MPC-based coatings confer excellent biocompatibility on medical implants such as coronary stents and MPC is also widely used in the manufacture of low irritation soft contact lenses. Now Ishihara and co-workers report that statistical copolymers comprising MPC and a hydrophobic comonomer (*n*-butyl methacrylate) aggregate in water to form micelles of approximately 20 nm in diameter which can be used to solubilise hydrophobic fluorescent probes [37]. Thus, these MPC-based surfactants, which were prepared by conventional free radical copolymerisation chemistry, may allow better protocols to be developed for the efficient delivery of hydrophobic drugs. The same Japanese group showed that related statistical copolymers based on MPC and styrene were effective blocking agents (i.e. non-specific antibody adsorption was suppressed) in ELISA-type immunoassays [38]. In collaboration with Biocompatibles (Farnham, UK) we have recently shown that MPC can be polymerised with excellent control in either water or methanolic solution via ATRP [39]. This breakthrough allows the synthesis of a wide range of well-defined, stimuli-responsive MPC-based diblock copolymers of narrow molecular weight distribution. Systematic studies of the biocompatible properties conferred by these surfactants are ongoing.

There is growing recognition of the commercial potential of sugar surfactants [40] and, by logical extension, glycopolymers. Fukuda's group reported the preparation of vinyl-functionalised sugar residues and their subsequent polymerisation by living radical chemistry [41]. Usually protecting groups are utilised to mask the hydroxy groups but with the development of aqueous ATRP there seems to be no intrinsic reason why protecting group chemistry should be necessary. Indeed, there is at least one literature example of the direct polymerisation of an unprotected mannose-based monomer under aqueous emulsion conditions at 55°C using ring-opening methathesis polymerisation (ROMP) [42]. Such polymers are potentially useful as 'multivalent ligands' in biological applications. Further advances are anticipated in this area in the near future.

9. Summary

Recent advances over the last 12 months or so suggest that there is much scope for the synthesis of a

wide range of well-defined, controlled-structure polymeric surfactants with various architectures. One of the more promising and versatile approaches appears to be living radical polymerisation chemistry, particularly ATRP. Such tailor-made surfactants are expected to find use in many diverse areas, including the preparation of new colloidal nanostructures, novel latex stabilisers and emulsifiers and various biomedical applications.

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