Novel nonionic polymerisable surfactants based on sulfoxides. 1. Monomer synthesis and general surfactant behaviour

Abstract  The synthesis, surface activity, and micellisation of a series of new nonionic polymerisable surfactants, often referred to as surfimers, are described. These monomers bear terminal vinyl groups or acrylic esters, and the nonionic sulfoxide moiety. Compared to many other nonionic hydrophilic fragments, the sulfoxide group behaves as a strongly hydrophilic fragment of small volume, that can balance up to an acryloyloxystearyl hydrophobic chain. The incorporation of the polar acrylate moiety at the end of the hydrophobic chain seems to confer surfactant properties similar to the ones of bola amphiphiles to the monomers.

Key words  Polymerisable surfactants · Alkyl sulfoxides · Monomer synthesis · Surfers

Introduction

Much work has been devoted in the past 2 decades to polymerisable surfactants (frequently referred to as “surfers”), often in the context of reactive emulsifiers for emulsion polymerisation and related processes [1–3]. Also, polymerisable surfactants have served as chemically well defined building blocks for the construction of the so-called “polyssoaps” [1, 4, 5]. Polyssoaps present a special class of micellar polymers which can be visualised as a necklace of laterally linked, individual surfactant fragments. The surfactant fragments can be anchored to the polymer backbone at different positions: via the hydrophilic head group (the so-called “head type”), via the end of the hydrophobic chain (the so-called “chain-end type”), or via a position in the midst of the hydrophobic chain (the so-called “mid type”). These different geometries give rise to strongly differing properties even for isomeric polymers [1, 5, 6]. As polymerisable surfactants are typically hygroscopic, free-radical polymerisation is the method of choice and, therefore, most known compounds bear a vinyl or a vinylidene moiety as the polymerisable group [1]. The high density of substituents on the backbone of such polymers results in severe steric crowding [7, 8], and thus generally, water-soluble homopolymers are only obtained from polymerisable surfactants of the “chain-end type” [1, 5–8].

Surfactants and polyssoaps are classified according to the nature of their hydrophilic group in three subclasses; namely, ionic ones, zwitterionic ones, and nonionic ones. Although ionic, in particular anionic, polymerisable surfactants and the corresponding polymers have found the most practical interest so far [1, 2], they are much less suited for model studies than the other classes. This is a consequence of the inherent problems in the investigation of polyelectrolytes. In the past we therefore focused on uncharged polymerisable surfactants and the corresponding micellar polymers, namely such bearing zwitterionic groups [5, 7, 8]. These polymers enabled us to perform a series of fundamental studies, so some basic relationships between the polymer geometry and the polarity of backbones, and key properties such as surface activity, solubilisation capacity, and emulsifying power could be established.

Although zwitterionic polyssoaps proved to be suited for fundamental studies, they are not ideal candidates. Often, they are difficult to synthesise in pure form, and
their solubility is low. Also, polyzwitterions are still sensitive to small amounts of added salts [9, 10], though the effects observed differ from the ones observed for polyelectrolytes. In fact following similar reasoning, nonionic polymerisable surfactants have attracted interest for fundamental studies since the early days [6, 11, 12], because their solubilities are often high and the sensitivity to added salts is low. Moreover, the “classical” nonionic groups are oligo(ethylene oxide) which can be easily prepared even on an industrial scale; however, such polymerisable surfactants present their own drawbacks. Oligo(ethylene oxide) are rather weakly hydrophilic groups only, and thus very voluminous: about two -O-CH₂-CH₂- fragments are needed to balance three -CH₂- groups [13, 14] in order to obtain water-soluble products. The ratio of the hydrophilic volume to hydrophobic volume is therefore at least 2:1, and is often much higher. Moreover, oligo(ethylene oxide) surfactants suffer from limited solubility at elevated temperatures owing to the occurrence of a lower critical solution temperature [13]. Also, long oligo(ethylene oxide) fragments are usually mixtures, rendering the discussion of experimental results in fundamental studies difficult. Additionally, the micellar polymers obtained tend to become insoluble with time, presumably owing to cross-linking by attack of oxygen on the numerous -CH₂-O- groups.

Still, studies on alternative nonionic surfactants are rare. They mainly comprise oligomers of oxazolines [15, 16], which share many problems with their poly(ethylene oxide) analogues, or derivatised sugars [17]. The latter are generally complicated to synthesise in pure form, and suffer from limited solubility in water in many cases owing to strong hydrogen bonding [18–20]. Moreover, they still present a rather unfavourable ratio of the hydrophilic volume to the hydrophobic volume, as normally about one -CHOH- fragment is required for two -CH₂- groups in order to obtain water-soluble products [13, 17].

Though often neglected, there are a variety of very small, nonionic hydrophobic groups, such as aminoxides, sulfoxides, phosphinooxides, and arsinoxides [21, 22]. The latter two groups are difficult to prepare when bearing additional functional fragments, but the first two groups are well accessible by various methods. Yet, amine oxides tend to inhibit free-radical polymerisation. Therefore, we explored the sulfoxide group as a small nonionic polar group for its use as an alternative head group for polymerisable surfactants. As the sulfoxide group is much more hydrophilic than a single ethylene oxide group [23], the head group can be much smaller than in oligo(ethylene oxide) surfactants. This is also true in comparison with the newly emerging nonionic surfactants based on sugars (see earlier). For example, an octyl chain is balanced by one sulfoxide group only, whereas this hydrophobic group typically requires six ethylene oxide units or one hexose unit [24]. Also, owing to the uncharged character, we expected strongly improved solubilities of sulfoxides compared to zwitter-ionic analogues in most solvents. Additional aspects, such as the potential chirality of the unsymmetrically substituted sulfoxide group, might offer some additional future perspectives.

**Experimental**

**Methods**

Elemental analysis was done at the University College of London. NMR spectra were recorded with Gemini 200 and 300 spectrometers (Varian). IR spectra were recorded with a FTS 135 IR Fourier transform spectrometer (BioRad). Surface tensions were measured with a manual tensiometer (Krüss 8501, De Noyé) at 21 ± 1 °C. Monomer solutions were equilibrated for 24 h before the measurements. Differential scanning calorimetry was performed with a PerkinElmer DSC7, applying heating and cooling rates of 2 °C/min.

**Materials**

The water used for all the experiments was purified by an Elgastat water purification system (resistance 18 MΩ). “Flash” column chromatography was performed on silicagel (Merck 230–400 mesh), or if stated explicitly, on Al₂O₃ (Acros, basic, 150 mesh). A small amount of the inhibitor di-t-butyl-p-cresol was added to all the reaction mixtures containing polymerisable components, but not to the final products.

**Dodecyl methyl sulfoxide (1)**

Dimethyl sulfate (11.00 g, 0.087 mol) was slowly added to n-dodecanthiol (19.22 g, 0.095 mol) and KOH (5.43 g, 0.092 mol) in 20 ml ethanol under a nitrogen atmosphere. The mixture was stirred for 72 h, producing a white precipitate. After addition of 100 ml water, the aqueous phase was extracted three times with CH₃Cl. The organic phases were combined, washed with 100 ml water, dried with sodium sulfate, and evaporated. Yield: 14.2 g (71%) dodecyl methyl thioether as a colourless liquid. n²₅ = 1.4583.

¹H NMR (200 MHz, CDCl₃, δ): 2.45 (t, 2H, -CH₂-S-), 2.05 (s, 3H, -S-CH₃), 1.55 (m, 2H, -CH₂-C-S-), 1.40–1.15 [m, 18H, -(CH₂)₂-], 0.85 (t, 3H, -CH₃-).

¹³C NMR (50 MHz, CDCl₃, δ): 34.0 (CH₂-CH₂-CH₂-CH₂-S-), 32.0 (CH₂-CH₂-CH₂-S-), 30.3, 30.0 [(CH₂)₂], 28.9 (CH₂-S-C-S-), 23.0 (CH₃-CH₂-), 15.6 (S-CH₃), 14.0 (CH₂-).

A solution of magnesium monoperoxyphthalate (1.52 g, 3.07 mmol) hexahydrate and of a few milligrams tetraxylammonium chloride in 10 ml water was added to dodecyl methyl thioether (1.00 g, 4.62 mmol) in 10 ml CH₂Cl₂. After 6 h of stirring at 40 °C, the organic phase was separated, washed twice with 10 ml water, dried over sodium sulfate, and evaporated. The crude dodecyl methyl sulfoxide was recrystallised from water and purified by flash chromatography (eluant: ethyl acetate) to remove traces of sulfoxide formed. Yield: 0.25 g (23%) as a colourless crystals, m.p.: 62 °C.

¹H NMR (200 MHz, CDCl₃, δ): 2.70 [m, 2H, -CH₂-S(=O)-], 2.54 [s, 3H, -(S(=O)-)CH₃], 1.70 [m, 2H, -(CH₂)-C-S(O)-], 1.40–1.15 [m, 18H, -(CH₂)₂-], 0.85 (t, 3H, -CH₃-).

¹³C NMR (50 MHz, CDCl₃, δ): 54.9 [-(CH₂)-S(=O)-], 38.6 [-(S(=O)-)CH₃], 31.9 (CH₂-C-CH₂-), 29.9, 29.3, 29.2 [-(CH₂)-], -CH₂-C-S(O)-], 28.8 (CH₂-C–C-S–), 22.5 (CH₃-CH₂-), 14.1 (CH₂-).