

Synthesis of novel cationic polymeric surfactants

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Abstract

A series of new cationic polymeric surfactants, comprising a short hydrophobic *n*-alkyl (C₁₂ or C₁₆) end-group and a long hydrophilic sequence of 17–68 2-(dimethylamino)ethyl methacrylate (DMA) units, were successfully synthesized by oxyanion-initiated polymerization. A previously titrated solution of DMSO⁻K⁺ was used for quantitative formation of the potassium alcoholate initiators from the corresponding C₁₂ or C₁₆ alcohols. Optimum polymerization conditions were found to be at or above room temperature, using THF as solvent. Under these conditions the polymers had relatively narrow polydispersities ($M_w/M_n \approx 1.25$) and both GPC and NMR spectroscopy showed no residual monomer. NMR studies of the surfactants in CDCl₃ also confirmed that good control over the degree of polymerization was achieved, indicating very high initiator efficiency. Cloud points of aqueous solutions of selected polymeric surfactants were determined by turbidimetry and decreased with increasing DMA chain length, as expected.

NMR spectra of the surfactants were also recorded in D₂O. The C₁₂ surfactants each had roughly the same degree of polymerization of DMA in D₂O as that obtained in CDCl₃, suggesting molecular dissolution. In contrast, the apparent degrees of polymerization for the DMA blocks in the C₁₆ surfactants were markedly higher in D₂O than in CDCl₃. This indicates reduced solvation for the C₁₆ moiety, which is consistent with micelle formation. Surface tensiometry studies indicated higher surface activities for the C₁₂-based surfactants compared to the C₁₆-based surfactants. Again, this is consistent with the hypothesis that the latter surfactants form intermolecular micelles in aqueous solution, whereas the C₁₂-based surfactants are molecularly dissolved. Dynamic light scattering and transmission electron microscopy studies confirmed the existence of micelles in C₁₆ surfactant solutions but no micelles were observed for the C₁₂ surfactants. Finally, a selectively deuterated C₁₂-based polymeric surfactant was also prepared for planned neutron reflectivity studies at the air–water interface. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cationic polymeric surfactants; Oxyanionic polymerization; NMR spectroscopy

1. Introduction

Surfactants are among the most versatile products used in the chemical industry, appearing in such diverse products as motor oils, pharmaceuticals and detergents. More recently, applications have been extended to such high-technology areas as electronic printing, magnetic recording, and biotechnology [1]. There are four classes of surfactants: (a) anionic, where the head group of the molecule has a negative charge; (b) cationic, where the head group bears a positive charge; (c) zwitterionic, where both positive and negative charges are present; and (d) non-ionic, where the

head group has no ionic character. Cationic surfactants, which are most relevant to the present study, usually fall into one of the following categories: long-chain amines or polyamines and their respective salts, quaternary ammonium salts (e.g. hexadecyltrimethyl ammonium bromide), oligo(ethylene oxide) amines and their quaternized derivatives, and amine oxides. Cationic surfactants are used in many applications from fabric softeners and toiletries to adhesion promoters in asphalt and corrosion inhibitors [2].

Living polymerization is an excellent and well-established method for controlling copolymer architecture and obtaining narrow molecular weight distributions [3–8]. In the case of poly(meth)acrylates, a wide range of materials can be synthesised with many different properties and potential applications. However, classical anionic polymerization of meth(acrylates) suffers from some severe limitations. One disadvantage is that “livingness” is often only achieved at or below 0°C with carbanionic initiators such as *n*-BuLi [9]. At room temperature, group transfer polymerization (GTP) is a well-established method for the

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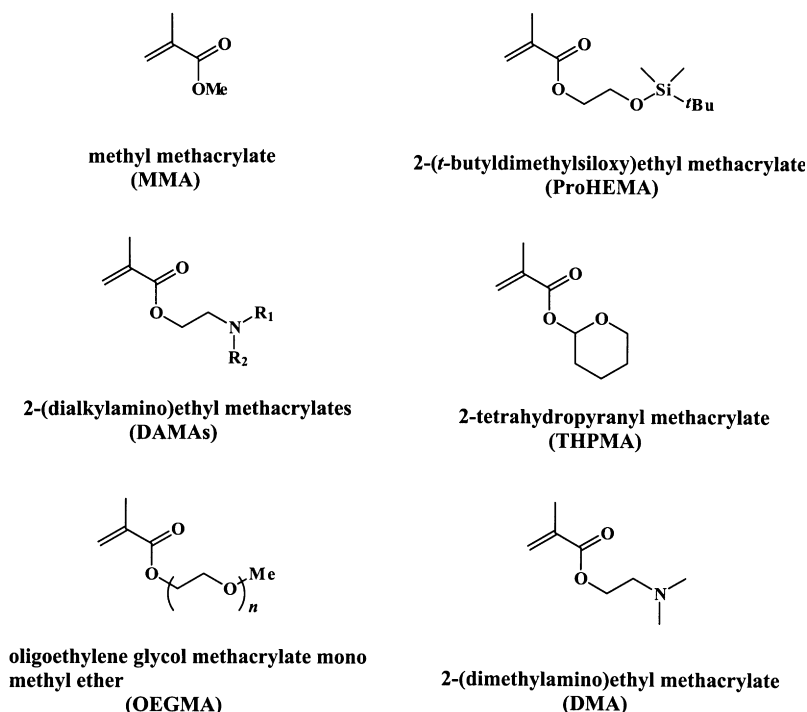


Fig. 1. Chemical structures of some methacrylate monomers employed in oxyanionic polymerizations.

synthesis of methacrylate polymers. However, one disadvantage of GTP is that a relatively expensive initiator is required, typically 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS).

The oxyanionic polymerization of methacrylates was first reported by Tomoi et al. [10], who used various alkali metal alkoxides to polymerize methyl methacrylate (MMA). For lithium and sodium alkoxides, it was shown that polymerization required the addition of aprotic dipolar co-solvents such as hexamethyl phosphoramide (HMPA) or DMSO. However, if *potassium* 2-methoxyethoxide was utilized as an initiator, polymerization proceeded to high yield (93%) in toluene at 0°C in the absence of any co-solvent. Unfortunately, in this early study no attempt was made to establish the livingness (or otherwise) of such oxyanionic polymerizations. More recently, Iijima et al. reported [11] the polymerization of 2-(*t*-butyldimethylsiloxy)ethyl methacrylate (ProHEMA derivative) (see Fig. 1) initiated by potassium ethoxide in THF at various temperatures. However, the initiation efficiency was only 67%, leading to imprecise control over the final polymer molecular weight. In later work the same group reported the synthesis of some 2-(diethylamino)ethyl methacrylate (DEA) homopolymers initiated by potassium ethoxide, and also DEA macromonomers using potassium 4-vinylbenzyl alcoholate as initiator [12]. In this study, better molecular weight control was achieved, particularly if these polymerizations were carried out at ambient temperature. Complex formation between the potassium cation and the monomer was suggested, implying increased nucleophilicity of the alcoholate anion. It was postulated [12] that a suitable heteroatom (oxygen or

nitrogen) in the β -position in the ester moiety is essential for the effective complexation of the cation.

Lascelles et al. [13] synthesized a series of water-soluble macromonomers based on 2-(dialkylamino)ethyl methacrylates (see Fig. 1) using various potassium alcoholates as initiators. Their findings were in general agreement with those of Nagasaki et al. regarding the requirement of an electronegative heteroatom (in this case nitrogen) joined to the β -position in the ester moiety. For example, no polymerization of 2-tetrahydropyranyl methacrylate (THPMA) (see Fig. 1) was observed, since the oxygen heteroatom of this monomer is attached to the α -carbon of the ester group. However, this hypothesis does not account for the lack of success obtained with oligo(ethylene glycol) methacrylate monomethyl ether or, indeed, for the uncontrolled, non-living polymerization of methyl methacrylate observed by Lascelles et al. The nature of the counter-ion is another important parameter: it was found that sodium alcoholates could not initiate the polymerization of DMA under the same conditions. This is in agreement with Tomoi et al., who found that sodium alcoholates only initiated polymerization when an aprotic dipolar cosolvent such as HMPA or DMSO, was used. We have recently extended the scope of ixyanion-initiated polymerization by employing potassium alcoholate macroinitiators such as PEO, PPO or PDMS [14–16]. For example, Vamvakaki et al. polymerized various tertiary amine methacrylates using PEO- and PPO-based macroinitiators. However, macroinitiator contamination was often observed by GPC due to incomplete initiation.

In the present work we have synthesised new low molecular weight cationic polymeric surfactants by oxyanionic

polymerization. The hydrophilic/hydrophobic nature of these surfactants can be compared to the non-ionic analogues reported by Ameri et al. [17] and by Patrickios et al. [18]. In our case the hydrophobic component is an aliphatic straight-chain of 12 or 16 carbon atoms (1-dodecanol, 1-hexadecanol) and the hydrophilic component, is a low molecular weight water-soluble polymer based on 2-(dimethylamino)ethyl methacrylate (DMA). The main aims of this work were: (1) to study the scope and limitations of oxyanion-initiated polymerization at different temperatures; (2) to synthesize new polymeric cationic surfactants and to study their aqueous solution properties (e.g. surface activity, micellar behaviour etc.); and (3) to prepare a selectively deuterated surfactant in order to carry out detailed neutron reflectivity studies on copolymer layers absorbed at the air–water interface.

2. Experimental

The chemicals were purchased from Aldrich. 1-Hexadecanol was re-crystallized from diethyl ether. THF was dried over sodium wire and then refluxed with potassium metal for three days and freshly distilled prior to use. The monomer was passed through a basic alumina column, stirred for 12 h in the presence of calcium hydride and 2,2-diphenyl-1-picrylhydrazyl hydrate inhibitor. It was stored under nitrogen at -9°C , and distilled before each polymerization. All other chemicals were used as received.

The polymerizations were conducted in anhydrous, inert conditions. All the glassware was stored for 12 h at 200°C and flamed out immediately after assembly. Liquid reagents were handled using standard schlenk techniques.

2.1. Surfactants synthesis using potassium hydride (KH)

A suspension of potassium hydride in mineral oil was placed in a dry pre-weighed schlenk. The mineral oil was removed by three extractions with *n*-pentane, which was added via cannula. All solvent was removed from the potassium hydride and the exact amount of potassium hydride (54 mg, 1.33 mmol) was found by weighing under nitrogen. The polymerization solvent (150 mL THF or DMSO) was added and the suspension was cooled to 0°C . A stoichiometric amount of alcohol was then added and the reaction mixture was stirred for 2 h at room temperature. Both potassium 1-dodecanolate and 1-hexadecanolate were insoluble in THF. The freshly distilled monomer was added quickly to the reaction mixture and the polymerizations were allowed to proceed for 1–3 h, depending on reaction conditions. The appearance of a yellow colour was observed, along with an exotherm of approximately 15°C for each polymerization conducted at ambient temperature. Termination of these polymerizations was accomplished by the addition of degassed methanol (2 mL). The resulting polymeric surfactants were isolated by filtration of the reaction mixture and concentrated under vacuum. The polymers

were further purified by dissolving in dilute acid, stirring with *n*-hexane (30 min), and then precipitated. Isolation of the surfactant as a tacky solid was achieved by the addition of potassium hydroxide up to pH 8, followed by salting out from the aqueous solution using sodium chloride. The residues were dissolved in dichloromethane, dried with sodium sulfate and concentrated under vacuum. The pure polymeric surfactants were finally vacuum-dried at room temperature overnight. Overall yields were greater than 90%.

2.2. Surfactant synthesis using potassium methylsulfinyl carbanion ($\text{DMSO}^{-}\text{K}^{+}$)

Potassium hydride (898 mg, 22.4 mmol), obtained as described above, was suspended in THF (35 mL). The suspension was cooled to 0°C with an ice bath before addition of dimethyl sulfoxide (DMSO, 3.5 mL, 2 molar excess). The suspension was allowed to warm up to room temperature and stirred until all the potassium hydride had reacted; this was evident due to the formation of a homogeneous phase. This $\text{DMSO}^{-}\text{K}^{+}$ solution was then used to generate the potassium alcoholate. The solution prepared was titrated against 2-naphthol in THF under inert atmosphere using triphenylmethane as indicator (5 mg) [19]. The end-point of the titration was easily observed by a bright red colour, indicating the formation of triphenylmethyl carbanion [20]. The concentration of the $\text{DMSO}^{-}\text{K}^{+}$ solution can be determined by addition of a 10 mL aliquot of this solution to water and titrating the potassium hydroxide liberated with a standardized HCl solution, using phenolphthalein as an indicator.

The potassium alcoholate initiators were formed in THF, from the corresponding *n*-alcohols, by treating with a stoichiometric amount of the previously titrated solution of $\text{DMSO}^{-}\text{K}^{+}$ for 2 h, first at 0°C , and then at 30°C . The DMA monomer was then added quickly via cannula to the stirred suspension. Clean-up was achieved as in 2.1.

2.3. Gel permeation chromatography

GPC was performed with a Viscotek gel permeation chromatography apparatus equipped with a Polymer Laboratories PL gel $3\ \mu\text{m}$ Mixed “E” column using THF as eluent. A Knauer refractive index detector K-3201 was used in series with a Knauer K-2501 ($\lambda = 254\ \text{nm}$) UV detector. The flow rate was $1.0\ \text{mL}\ \text{min}^{-1}$. The number-average molecular weights (M_n) and polydispersity indices (M_w/M_n) were calculated relative to PMMA standards ranging from 625 to $29,400\ \text{g}\ \text{mol}^{-1}$.

2.4. Nuclear magnetic resonance spectroscopy

A Bruker 300 MHz instrument was used to acquire the ^1H and ^{13}C NMR spectra of polymer solutions in CDCl_3 , D_2O or d_8 -toluene.

Table 1

Experimental data for the synthesis of the new cationic polymeric surfactants (reaction conditions: solvent, THF; reaction time: 60–120 min; [initiator] = 0.01 M; [monomer] = 0.67–0.85 M)

Entry	Potassium alcoholate	Base	Temp. (°C)	Theoretical		Experimental		
				DP	M_n (g mol ⁻¹)	M_n (g mol ⁻¹) ^a	DP ^a	M_w/M_n ^b
I	C ₁₆ -O ⁻ K ⁺	KH	22	30	5000	5700	35	1.22
II	C ₁₆ -O ⁻ K ⁺	KH	50	64	10,300	–	–	1.34
III ^c	C ₁₆ -O ⁻ K ⁺	DMSO ⁻ K ⁺	0	63	10,100	–	–	1.92
IV	C ₁₆ -O ⁻ K ⁺	DMSO ⁻ K ⁺	22	64	10,300	10,600	66	1.25
V	C ₁₆ -O ⁻ K ⁺	DMSO ⁻ K ⁺	50	65	10,500	9400	58	1.30
VI ^d	C ₁₆ -O ⁻ K ⁺	DMSO ⁻ K ⁺	50	18	3100	2900	17	1.28
VII ^e	C ₁₂ -O ⁻ K ⁺	KH	22	63	10,000	–	–	1.31
VIII	C ₁₂ -O ⁻ K ⁺	DMSO ⁻ K ⁺	50	66	10,600	10,900	68	1.19
IX ^d	C ₁₂ -O ⁻ K ⁺	DMSO ⁻ K ⁺	22	43	6900	6600	41	1.29
X ^d	d ₂₅ C ₁₂ -O ⁻ K ⁺	DMSO ⁻ K ⁺	50	18	3000	3000	18	1.42

^a Determined by ¹H NMR.

^b Determined by GPC.

^c The GPC chromatogram gave a bimodal signal.

^d Triphenylmethane was used as indicator for the quantitative formation of the alcoholate initiator.

^e The polymerization solvent was DMSO.

2.5. Surface tensiometry

Surface tension (γ) measurements were carried out using a Krüss K10ST surface tensiometer and a platinum ring. All measurements were carried out at 20°C. Reproducibility was checked by frequent determination of the surface tension of de-ionized doubly-distilled water (72–73 mN m⁻¹).

2.6. Cloud points

These were determined by monitoring the optical density at 500 nm of a stirred 1.0% w/v polymeric surfactant solution with increasing temperature, using a Lambda 2S UV–Vis spectrometer.

2.7. Dynamic light scattering

These measurements were carried out on 1.0 w/v % copolymer solutions at pH 4.0–9.5, using a Malvern PCS 4700 spectrometer equipped with a 80 mW argon ion laser operating at 632.8 nm. The data were fitted using monomodal

cumulants analysis. Measurements were made at an angle of 90° to the incident beam.

2.8. Transmission electron microscopy

TEM studies were carried out using a Hitachi 7100 instrument operating at 75 kV. Negative staining using uranyl acetate was employed in order to improve the contrast.

3. Results and discussion

It is generally accepted that the three most important characteristics of a “living” polymerization are: (1) a linear increase in molecular weight with conversion; (2) narrow polydispersities; and (3) block copolymer formation. We have carried out detailed studies for the oxyanionic polymerization of DMA using potassium benzyl alcoholate as initiator [16]. The number-average molecular weight increased linearly with conversion and the polydispersity remained low throughout the polymerization. Furthermore, diblock and triblock copolymers were readily obtained with

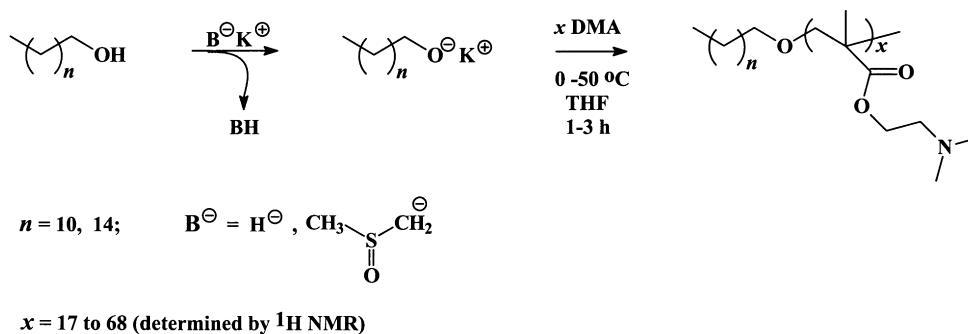


Fig. 2. Reaction scheme for the synthesis of polymeric surfactants via the oxyanionic polymerization of DMA using potassium *n*-alkyl alcoholate initiators.

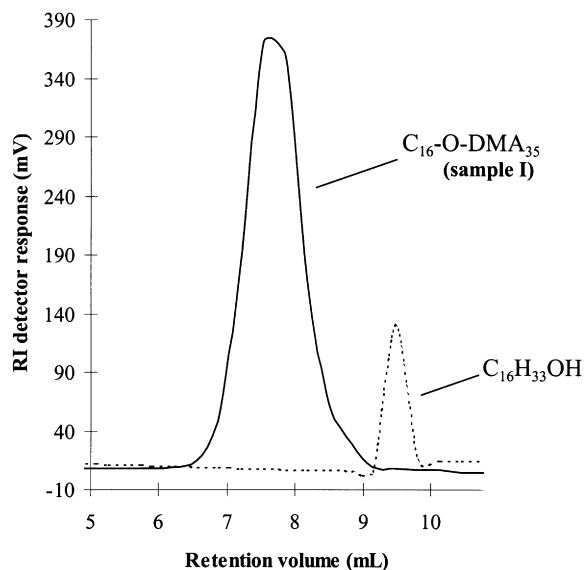


Fig. 3. GPC RI detector response for surfactant I overlaid with $C_{16}H_{33}OH$.

excellent control over the overall block compositions [16]. Thus the living nature of the oxyanionic polymerization of DMA has already been established.

In earlier work incomplete initiation efficiency was encountered, therefore our first aim was to ensure quantitative formation of the potassium alcoholate initiator. The first polymeric surfactants synthesized in the present work (summarized in Table 1) were prepared using potassium hydride to form the alcoholate initiator (see Fig. 2). Ideally, the synthesis of the potassium alcoholate initiators must be performed in the absence of excess alcohol, which could otherwise terminate some of the growing chains and hence broaden the molecular weight distribution. On the other hand, excess hydride anion (or $DMSO^-$) could itself initiate the uncontrolled polymerization of DMA and consequently generate DMA homopolymer contamination [13,16]. Problems were encountered in achieving precise reagent stoichiometry. Many experiments were carried out using KH but only three of these syntheses gave reliable

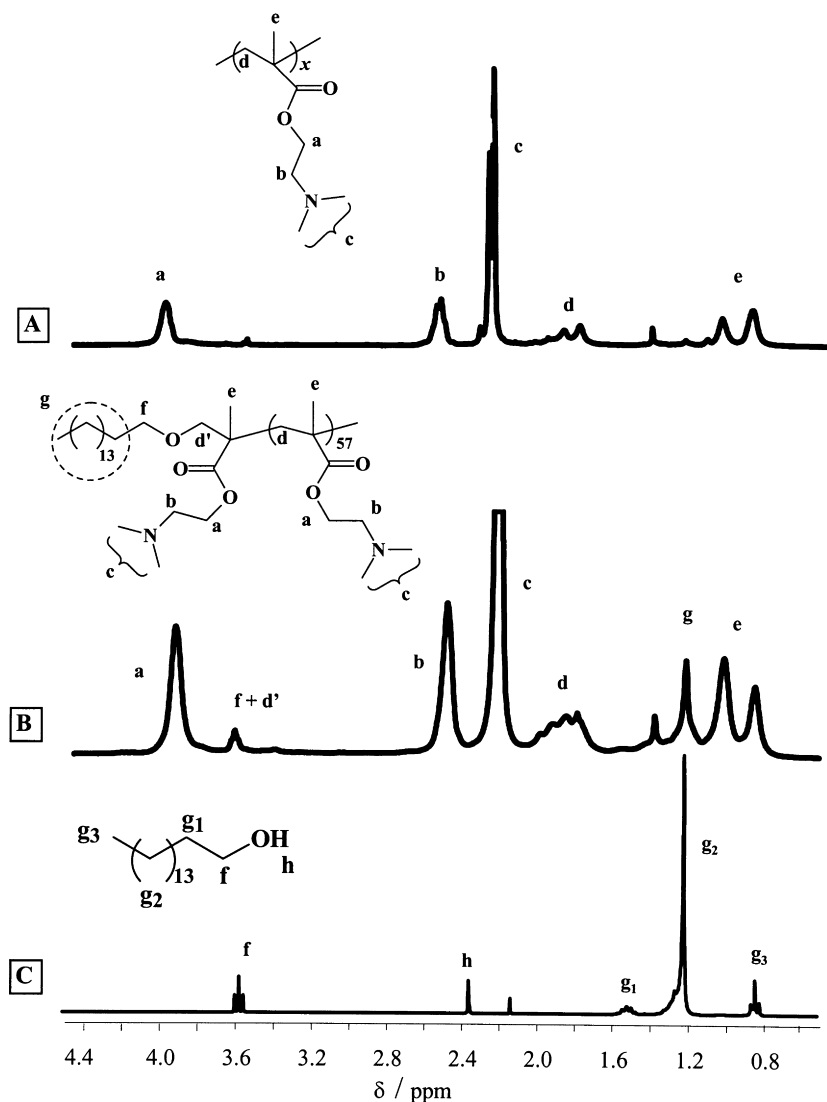


Fig. 4. 1H NMR spectra ($CDCl_3$, 300 MHz) of: (A) DMA homopolymer; (B) surfactant V; and (C) 1-hexadecanol.

Table 2

Apparent degree of solvation of the hydrophobic C₁₂ or C₁₆ components in selected polymeric surfactants by ¹H NMR in D₂O

Polymeric surfactant	Actual composition ^a	Apparent composition ^b	Apparent degree of solvation of <i>n</i> -alkyl chain in D ₂ O (%)
VIII	C ₁₂ -DMA ₆₈	C ₁₂ -DMA ₇₂	94
IX	C ₁₂ -DMA ₄₁	C ₁₂ -DMA ₅₁	84
V	C ₁₆ -DMA ₅₈	C ₁₆ -DMA ₈₇	76
I	C ₁₆ -DMA ₃₅	C ₁₆ -DMA ₆₆	67

^a ¹H NMR in CDCl₃ at 20°C.^b ¹H NMR in D₂O at 20°C.

block compositions and relatively low polydispersities (see Table 1, entries **I**, **II** and **VIII**). Lascelles et al. also used potassium hydride for generating the alcoholate initiator and reported similar problems [13]. In their case UV GPC analysis indicated contamination of the desired macromonomer with residual 4-vinylbenzyl alcohol, which suggested reduced initiator efficiency.

Alternative methods for achieving quantitative alcoholate formation were investigated. A well-established procedure for the quantitative titration of hydroxyl groups is the use of a potassium naphthalene complex [21]. In principle, the end-point of this reaction is easily determined. However, in practice both Nagasaki et al. and Vamvakaki et al. reported low initiation efficiencies and also some naphthalene contamination. Finally, Hillmyer and Bates [22] reported that an excess of potassium naphthalene is required to form the potassium alcoholate quantitatively. If correct, this would inevitably lead to naphthalene contamination and possibly also competing initiation from the excess potassium naphthalene complex.

In order to avoid the problems summarized above, DMSO⁻K⁺ solution was selected for the quantitative formation of the potassium alcoholate initiator (either potassium 1-dodecyl alcoholate or potassium 1-hexadecyl alcoholate) in the present work. A reaction scheme is shown in Fig. 2. DMSO⁻K⁺ was chosen for converting the 1-hexadecanol and 1-dodecanol to their corresponding potassium alcoholate salts for several reasons. It is a strong base [23], it can be easily titrated using triphenylmethane as indicator to enable its exact concentration to be determined [20], DMSO⁻K⁺ solutions can be stored for long periods without decomposition [24] and the conjugate acid is DMSO, which is an aprotic, polar solvent well suited to nucleophilic reactions.

As previously discussed, although reasonable control in the synthesis of C₁₆-DMA and C₁₂-DMA can be achieved using KH as a base, reproducibility was generally poor. In contrast, the DMSO⁻K⁺ method is a much more reliable route to well-controlled block-copolymers. The reaction solvent was dry THF, apart from entry **VII**, where DMSO was used as solvent. It was thought that such an aprotic, polar solvent might be beneficial for these polymerizations and hence might lead to

narrower polydispersities. However, no such improvement was discernible.

It has been reported that, in some cases, oxyanionic polymerizations conducted at higher temperatures (e.g. 50°C), lead to narrower molecular weight distributions [12,13]. Hence the effect of varying the polymerization temperature was examined. Broader polydispersities were obtained at 0°C (see Table 1, entry **III**), indicating that the rate of initiation is significantly slower at this temperature. However, there were no discernible differences between polymerizations carried out at ambient temperature and those at 50°C.

The polymeric surfactants were characterized using both GPC and ¹H NMR spectroscopy. No residual DMA monomer was observed in the GPC traces, which is consistent with the high yields of recovered polymers. The GPC trace of each surfactant was well separated from that of the precursor *n*-alcohol (see Fig. 3). This indicates efficient initiation via the DMSO⁻K⁺ method, with little or no contamination from the residual initiator.

Fig. 4 shows the ¹H NMR spectra (CDCl₃, 300 MHz) of: (A) DMA homopolymer synthesized by oxyanionic polymerization; (B) polymeric surfactant **V**; and (C) 1-hexadecanol (the *n*-alcohol initiator used for preparing **V**). As expected, these NMR spectra confirm the presence of the 1-hexadecanol initiator fragment. Moreover, since the NMR signals due to this moiety are significantly broadened in spectrum (B) compared to those in spectrum (C), it must be covalently attached to the DMA chain of polymeric surfactant **V**. It is also worth noting that there are no traces of either DMA monomer or the 1-hexadecanol starting material in spectrum (B).

In order to determine the surfactant composition (i.e. the degree of polymerization of the DMA chains), the peak integral of signal **a** at δ 4.1 (corresponding to the oxymethylene protons of the DMA residues) was compared to that of signals **d**, **e** and **g** at δ 0.5–2.1 (corresponding to protons from both the DMA residues and the initiator fragment). The degrees of polymerization calculated from the NMR spectra are in very good agreement with those expected from the monomer/initiator molar ratios, as shown in Table 1. The complex signal at δ 3.6 is also noteworthy, due to the **d'** and **f** protons adjacent to the oxygen at the block junction point.

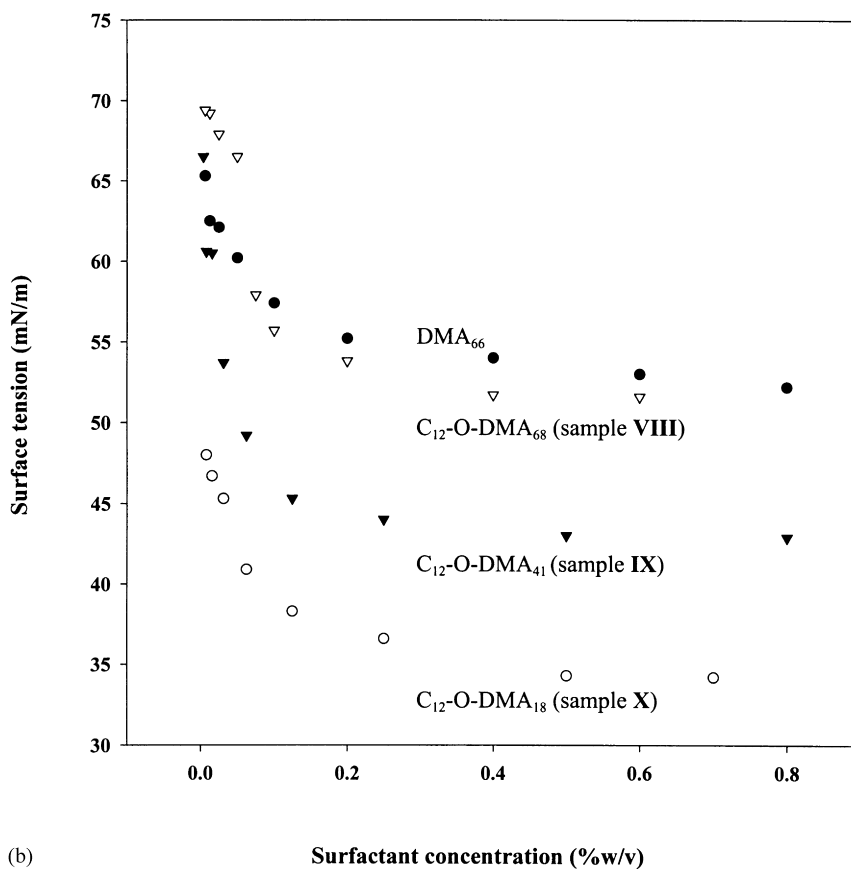
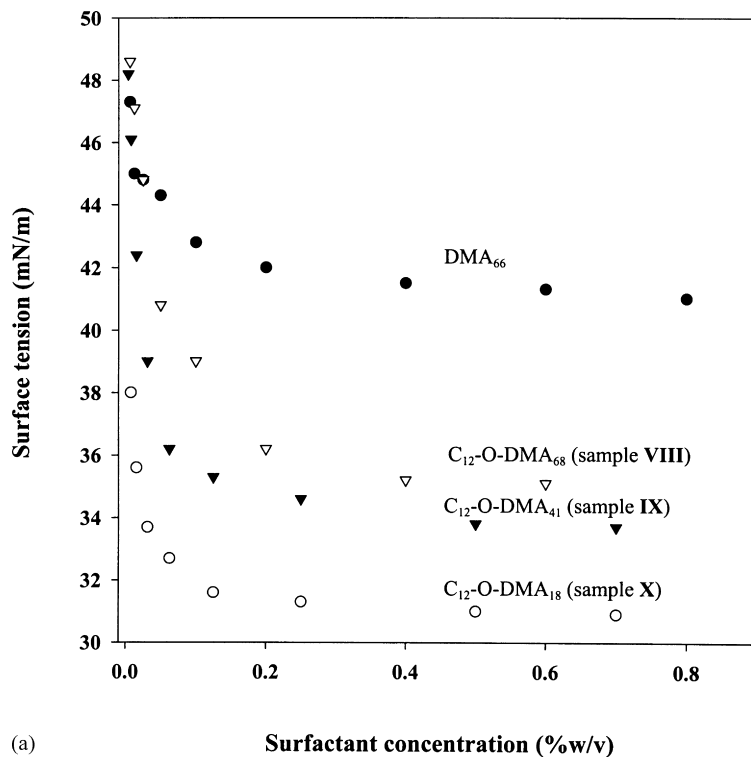


Fig. 5. Surface tensiometry curves as a function of copolymer concentration for selected C₁₂-based surfactants compared with DMA homopolymer: (a) at pH 9.5; and (b) at pH 6.0.

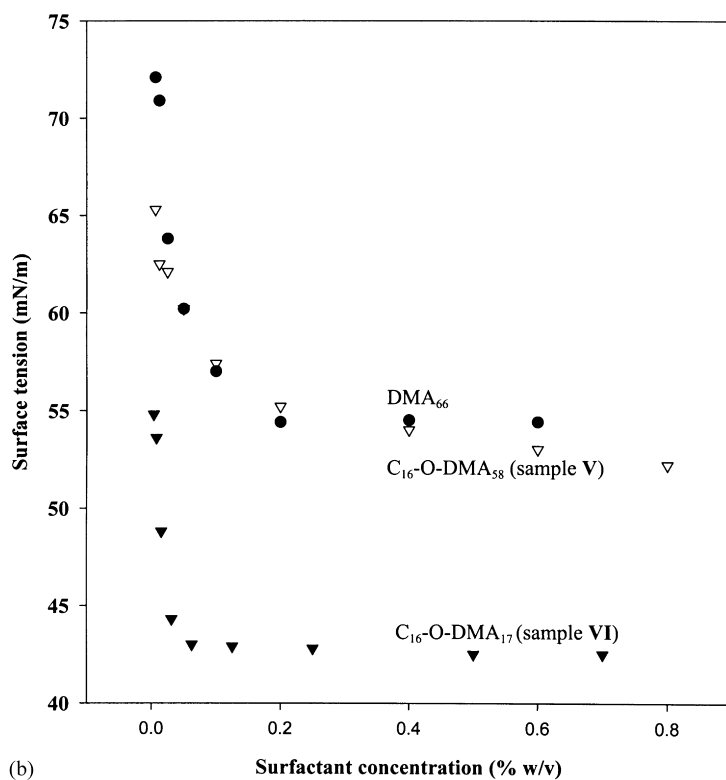
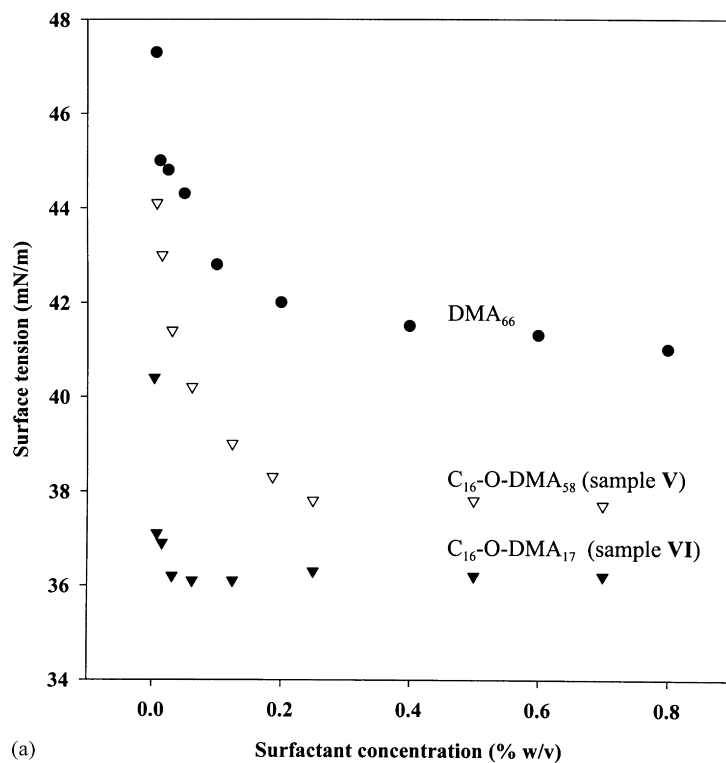


Fig. 6. Surface tensiometry curves as a function of copolymer for selected C₁₆-based surfactants compared with DMA homopolymer: (a) at pH 9.5; and (b) at pH 6.0.

We have also successfully synthesized a $C_{12}D_{25}O$ -DMA polymeric surfactant **X** by the same method. In this case there are no proton signals attributable to the deuterated C_{12} moiety. However, the degree of polymerization can nevertheless be estimated from its 1H NMR spectrum (D_2O) by comparing the peak integral at δ 3.6–3.7 due to the CH_2 of the *first* DMA residue (at the hydrophilic–hydrophobic junction point) to that at δ 4.3 due to the oxymethylene protons of *all* the DMA residues. This approach yields a degree of polymerization of 18 for the DMA chain, which is in exact agreement with the theoretical degree of polymerization for this surfactant. This selectively deuterated surfactant was prepared for a series of neutron reflectivity experiments, which are planned in the near future. The adsorption of this surfactant at the air–water interface will be studied as a function of pH using the method of contrast variation, which should lead to a detailed description of the structure of the surfactant monolayer. It should be particularly interesting to compare these results with those already reported for DMA–MMA diblock copolymers [25,26].

Selected NMR spectra were recorded in D_2O to assess the tendency of the C_{12} -DMA and C_{16} -DMA surfactants to form well-defined aggregate structures (i.e. micelles). In this medium the C_{12} surfactant series had approximately the same degrees of polymerization for the DMA block as those obtained in $CDCl_3$, as shown in Table 2. These data support the idea that, in D_2O , the C_{12} surfactants are *molecularly* dissolved. The same NMR experiments were carried out with the C_{16} surfactant series. Although the proton signals corresponding to the C_{16} component are still visible in D_2O , their integrated intensities (relative to the DMA residues) are significantly lower than those observed in $CDCl_3$. In other words, the C_{16} surfactants exhibited significantly higher *apparent* degrees of polymerization for the DMA chains in D_2O than in $CDCl_3$. This observation of reduced solvation for the hydrophobic C_{16} component in D_2O is consistent with the aggregation of the C_{16} surfactants in this medium to form intermolecular micelles. This interpretation is consistent with other experimental observations, as discussed below.

Cloud points were determined for 1.0% w/v aqueous solutions of selected polymeric surfactants at pH 9.5 using turbidimetry. Surfactants **I** and **V** have cloud points of 32.3 and 35.3°C, respectively. Comparing these values to those obtained for DMA homopolymers of similar molecular weight (43.2 and 40.7°C, respectively) it is clear that the hydrophobic *n*-alkyl chain aids inter-molecular aggregation of the DMA chains in aqueous media, thus lowering their cloud points. Also the cloud point reduction was more pronounced for the lower molecular weight DMA chain (surfactant **I**), as expected. The values obtained in this study are consistent with observations previously reported for non-ionic polymeric surfactants [17,18].

The surface tension curves obtained for selected polymeric surfactants are shown in Figs. 5 and 6. The hydrophobic *n*-alkyl chain imparts higher surface activity than

that of DMA homopolymer. For the C_{12} surfactant series the limiting surface tensions are remarkably low at pH 9.5 (Fig. 5a). For surfactant **X**, the limiting surface tension was as low as approximately 30.9 mN m^{-1} . The pK_a for DMA homopolymer is around 6.6 [27] so at this pH the DMA residues are almost completely deprotonated. As the degree of polymerization of the DMA chains is increased, the hydrophilic–hydrophobic balance of these surfactants is altered and their surface activities are reduced. Nevertheless, even at a degree of polymerization as high as 68 the limiting surface tension of surfactant **VIII** at pH 9.5 is still significantly lower than that of a DMA homopolymer with a similar degree of polymerization (see Fig. 5a).

Surface tensiometry studies were carried out on the same C_{12} surfactant series at pH 6 (Fig. 5b). Clearly, the limiting surface tensions are all appreciably higher at this pH, indicating lower surface activities. For example, the limiting surface tension at pH 9.5 was 34 mN m^{-1} for surfactant **IX**, while at pH 6 the corresponding value was 43 mN m^{-1} . The degree of protonation of the DMA chains affects the hydrophilic–hydrophobic balance of the polymeric surfactant, which in turn determines its surface activity. Thus, since the surfactant solubility is higher at pH 6, its adsorption at the air–water interface is reduced.

It is also noteworthy that the difference in surface activity for the same C_{12} surfactant at pH 9.5 and 6.0 greatly depends on the degree of polymerization of the DMA chains. For example, the increase in the limiting surface tension at pH 6 for surfactant **X**, which has a degree of polymerization of 18, was only 3.0 mN m^{-1} , while for surfactant **VIII** (degree of polymerization = 68), the increment was 17 mN m^{-1} .

Surface tensiometry studies were also carried out on selected C_{16} -DMA surfactants (Fig. 6). Since the hydrophobic alkyl chain is longer, higher surface activities (lower limiting surface tensions) were expected for a given degree of polymerization of the DMA block. However this surfactant series is actually less surface active than the C_{12} -based surfactants. For example, surfactant **VI** (C_{16} -DMA₁₇) had a limiting surface tension of 36 mN m^{-1} compared to 31 mN m^{-1} for surfactant **X** (C_{12} -DMA₁₈). The substantially lower surface activities (higher limiting surface tensions) exhibited by the C_{16} series can be explained if these surfactants, unlike the C_{12} series, form intermolecular aggregates (i.e. micelles) in aqueous solution. This hypothesis is consistent with our 1H NMR studies in D_2O and also with our transmission electron microscopy (TEM) studies (as discussed below).

At pH 6, the surface activity of surfactant **V** (C_{16} -DMA₅₈) is almost identical to that observed for a DMA homopolymer with a similar degree of polymerization. At a sufficiently high surfactant concentration micelle formation is expected in bulk solution. A 0.5% w/v aqueous solution of this surfactant at pH 6.0 was studied by dynamic light scattering (DLS). This technique indicated an intensity-average hydrodynamic diameter of approximately 270 nm. Similar DLS measurements were made on selected C_{12}

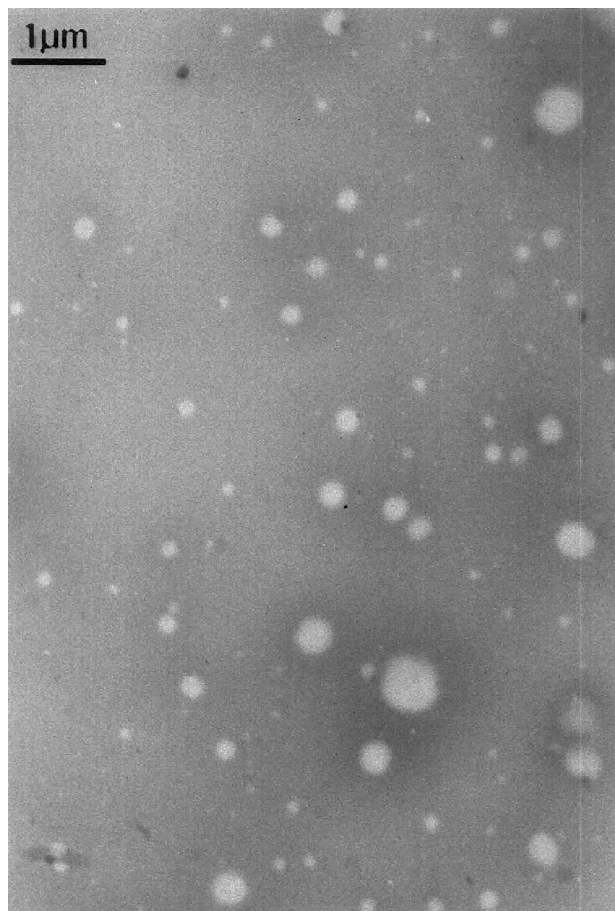


Fig. 7. Typical transmission electron micrograph of micelles prepared from a dilute aqueous solution of surfactant V (C_{16} -DMA₃₈) at 20°C.

surfactants (surfactants **VIII** and **IX**) and no micelles were detected. These results are in good agreement with the ^1H NMR observations discussed above.

Finally, micelle formation by the C_{16} -based surfactant was confirmed directly by examining dried, diluted aqueous solutions by TEM. Uranyl acetate was used to improve the contrast with the background. For surfactant **V**, a population of polydisperse spherical micelles with an average diameter of 250 nm was observed, as shown in Fig. 7. Allowing for polydispersity effects, this diameter is in reasonable agreement with that obtained by dynamic light scattering. In contrast, no micelles were observed by TEM when examining grids prepared by drying dilute aqueous solutions of the C_{12} -based surfactants.

4. Conclusions

Two series of new cationic polymeric surfactants have been synthesized by oxyanionic polymerization. These surfactants comprise a C_{12} or C_{16} alkyl chain as the hydrophobic component and a low molecular weight cationic block based on 2-(dimethylamino)ethyl methacrylate (DMA) as the hydrophilic component.

Using a previously titrated solution of DMSO^-K^+ for the formation of the potassium alcoholate initiator led to improved control over the oxyanionic polymerization of the DMA monomer. Optimum reaction conditions were found to be at room temperature or above, using THF as solvent. Under these conditions the polymers had relatively narrow polydispersities ($M_w/M_n < 1.25$) and GPC and NMR analyses showed no trace of monomer. NMR was also used to confirm that the actual degrees of polymerization of the DMA chains were very similar to those expected from the monomer/initiator ratios, indicating very high initiator efficiency.

Surprisingly, the C_{12} -based surfactants proved to be more surface active than the C_{16} -based surfactants. In both cases the limiting surface tensions depended on both the surfactant structure (i.e. the hydrophilic–hydrophobic balance) and also the solution pH. On the basis of our combined NMR, surface tension, dynamic light scattering and electron microscopy evidence we believe that the C_{12} surfactants are molecularly dissolved (or possibly form intramolecular micelles) in aqueous solution, whereas the C_{16} surfactants form intermolecular micelles. Finally, a deuterated surfactant ($C_{12}\text{D}_{25}\text{O}$ -DMA) was also prepared for a series of neutron reflectivity studies that are now in progress and will be reported in due course.

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