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Novel polymerizable mono- and divalent quaternary ammonium cationic surfactants: I. Synthesis, structural characterization and homopolymerization

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Eight novel polymerizable monovalent quaternary ammonium bromide surfactants and five model non-polymerizable structurally analogous surfactants have been synthesized. Methylation of free amine groups in six of the polymerizable monoquaternary ammonium species has yielded the corresponding divalent diquaternary ammonium dibromide surfactants, and likewise, five non-polymerizable divalent diquaternary ammonium dibromides have been prepared. All the new molecules have been characterized structurally by elemental microanalysis and ^{1}H nuclear magnetic resonance spectroscopy. The solubility, melting behaviour and homopolymerizability of the monomers have been evaluated and the results discussed with those of structurally related systems already in the literature. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymerizable surfactant; divalent surfactant)

INTRODUCTION

Interest in polymerizable surfactants has intensified in recent years as a result of the recognition of a number of potential technological advantages such surfactants might bring to, e.g. polymer emulsions, particulate encapsulation, etc. Polymerizable quaternary ammonium salt surfactants formed the basis of our own earlier studies[1,2] and relevant literature is cited therein. Recently we have also reported our results on polymerizable non-ionic surfactants[3], and again the relevant literature is reviewed in our publication. Since the latter work appeared three very useful review-type texts have been produced by Paleos and coworkers[4], Nagai[5] and Guyot and Tauer[6]. The latter offers broad coverage of the area and includes a discussion of surface active free radical initiators ('inisurfs'), surface active transfer agents ('transurfs') as well as polymerizable surfactants ('surfmers').

While these developments have occupied the time of polymer chemists, surface chemists themselves have been developing molecules with novel structures and unusual surface activity properties. For example, the size of the headgroup in quaternary ammonium surfactants and its effect on micellization has been examined by Buckingham *et al.*[7]. Dimeric surfactants, i.e. molecules with two headgroups and two hydrophobic tails have been further studied by Diamant and Andelman[8], while Nakatsuji and his group have examined species with two and three tails *each* with two headgroups, and most recently, molecules with three tails and three headgroups, i.e. a surfactant trimer[9]. With the latter sulfonate surfactants, the critical micelle concentration was found to increase with increasing chain length of the tails, i.e. the surface activity behaviour is reversed relative to the norm.

Divalent single chain surfactants (i.e. surfactants with a doubly charged headgroup either as a single 2+ or 2− charge, or with two + or two − charges localized closely together) have been known for many years, but have attracted largely only academic interest[10,11].

However, interest in these is expanding again[12] and possible technological advantages can be envisaged from using such species. We now report on the synthesis of a substantial group of polymerizable divalent diquaternary ammonium salt surfactants, (*Scheme 1*) and their structurally analogous polymerizable monoquaternary ammonium salts (*Scheme 2*). As far as we are aware this is the first premeditated study of this type, where ultimately we are seeking improved properties in polymer emulsions prepared with such surfactants. This manuscript (Part I) will describe the synthesis, structural characterization and homopolymerization of novel mono- and divalent species, while Part II (submitted to *Polymer*) covers the surface activity, use in emulsion polymerization and biocidal activity of these species.

EXPERIMENTAL

Materials

11-Bromoundecan-1-ol (Aldrich Chem. Co.) was recrystallized from hot petroleum ether (30–40°C).

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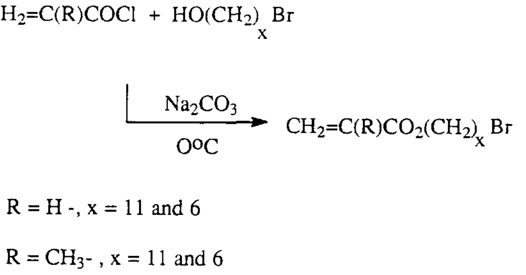


$$CH_2{=}C(R)COCl + HO(CH_2)_xBr \xrightarrow[0^{o}C]{Na_2CO_3} CH_2{=}C(R)CO_2(CH_2)_xBr$$

$$R = H\text{-}, x = 11 \text{ and } 6$$

$$R = CH_3\text{-}, x = 11 \text{ and } 6 \qquad (1)$$

N, *N*-Tetramethylethylenediamine (Aldrich Chem. Co.) was distilled then stored over 4 Å molecular sieves. Methacryloyl chloride (Fluka), acryloyl chloride (Aldrich Chem. Co.), trimethylamine (Fluka) (33% in ethanol), 1,4-dimethylpiperazine (Aldrich Chem. Co.) 4-[2-(dimethylamino)ethyl]morpholine (Aldrich Chem. Co.), 6-bromohexan-1-ol (Aldrich Chem. Co.), 1-bromodecane (Aldrich Chem. Co.), 1-bromododecane (Aldrich Chem. Co.), 1-bromohexadecane (Aldrich Chem. Co.), methyl bromide (Aldrich Chem. Co.), azobisisobutyronitrile (AIBN) (Aldrich Chem. Co.) and 2,2-dimethoxy-2-phenylacetophenone (DMPAP) (Aldrich Chem. Co.) were used as supplied. Other reagents and solvents were general purpose species and were used as supplied unless specified otherwise in preparations.

Analytical equipment

^{1}H nuclear magnetic resonance (n.m.r.) spectra were normally recorded on a Bruker WM250 MHz spectrometer. High field ^{1}H n.m.r. spectra were obtained on a Bruker 400 MHz instrument in a few cases to confirm chemical shift assignments. Elemental microanalyses were performed on a Perkin-Elmer Series II Elemental Analyser. Melting points were recorded using a Gallenkamp Digital Melting Point Apparatus.

Synthesis of ω-bromoalkanyl(meth)acrylates

These were prepared according to equation (1). A typical reaction was as follows.

1-Bromoundecan-1-ol (10.0 g, 0.04 mol) was dissolved in sodium dried ether (40 ml) in a one-necked round-bottomed flask fitted with a pressure equalizing dropping funnel with a drying tube. The flask was immersed in an ice-bath and stirred for 15 min. Sodium carbonate (6.0 g, 0.06 mol) was then added to the stirring solution. Finally, acryloyl chloride (3.95 g, 0.04 mol) in sodium dried ether (35 ml) was added dropwise to the stirring mixture over a period of 15 min. The mixture was stirred for a further 2 days. After filtering, the ether solution was washed three times with a 2% sodium hydrogen carbonate solution to remove unreacted acid chloride, and dried over magnesium sulfate. The dried solution was then passed through a short column of neutral alumina to remove unreacted alcohol. Thin layer chromatography (t.l.c.) (50:50 acetone/pet. ether) and infra-red spectroscopy (i.r.) were used to check the absence of starting materials. The weight of the viscous oily product obtained was 9.0 g (74%).

Experimental data for the other syntheses are summarized in *Table 1* along with the elemental microanalytical data for the products. *Table 2* summarizes the ^{1}H n.m.r. assignments.

Synthesis of polymerizable and non-polymerizable monoquaternary ammonium bromides, PMQI-VIII and MQI-V

These were prepared according to equation (2).

Typically 11-bromoundecanyl acrylate (5.86 g, 0.02 mol) along with *N*, *N*, *N'N'*-tetramethylethylenediamine (10.0 g, 0.09 mol) and a small amount of quinol to prevent spurious polymerization were stirred together in a round-bottomed flask at 50°C for 2 days. A yellow precipitate formed on addition of ether. The mixture was cooled in dry ice and the solid was washed several times with ether. Finally, it was filtered under nitrogen to yield a solid which became sticky on contact with air. The solid was recrystallized from ethyl acetate and filtered under nitrogen. It was then stored in a desiccator. The weight of product was 6.3 g (78%). The material was too deliquescent to determine a melting point.

In the case of PMQ-VII and VIII and MQI-V, recrystallization was from acetone and ethyl acetate, respectively, and melting points could be determined for these (see *Table 9* later).

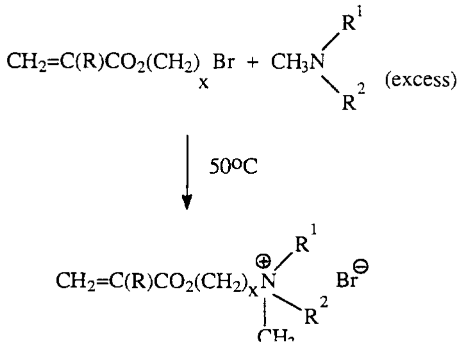
Experimental data for all these syntheses are summarized in *Table 3*, while *Table 4* contains the elemental microanalytical data. *Table 5* summarizes the ^{1}H n.m.r. assignments (see *Scheme 1* for structures).

Table 1 Preparation of ω-bromoalkanyl(meth)acrylates

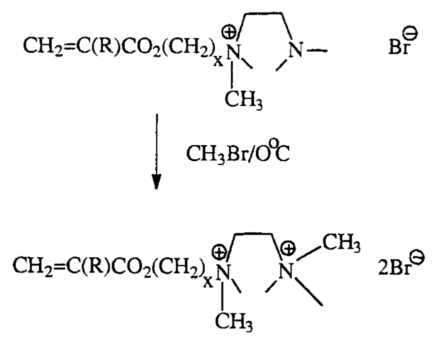
				Microanalytical data (%)					
				Calculated			Found		
Alcohol (g, mol)	Acid chloride (g, mol)	Weight of product (g)	Yield (%)	C	H	Br	C	H	Br
11-Bromoundecan-1-ol (10.0, 4.0 × 10^{-2})	Acryloyl chloride (4.0, 4.0 × 10^{-2})	9.0	74	55.1	8.3	26.2	55.3	8.3	24.7
11-Bromoundecan-1-ol (10.0, 4.0 × 10^{-2})	Methacryloyl chloride (5.2, 5.0 × 10^{-2})	10.0	79	56.4	8.6	25.3	56.9	8.6	27.9
6-Bromohexan-1-ol (4.5, 2.5 × 10^{-2})	Acryloyl chloride (3.0, 3.0 × 10^{-2})	5.2	89	46.0	6.4	34.0	45.3	6.2	34.4
6-Bromohexan-1-ol (4.5, 2.5 × 10^{-2})	Methacryloyl chloride (4.0, 4.0 × 10^{-2})	3.5	58	49.8	7.1	33.1	49.6	7.0	33.9

Table 2 ^1H n.m.r. assignments for the ω-bromoalkanyl(meth)acrylates, $CH_2 = C(R)CO_2CH_2CH_2^a(CH_2)_xCH_2^bCH_2Br$

Compound	^1H n.m.r. resonances in $CDCl_3$ (250 MHz)
11-Bromoundecylacrylate	δ 1.29 (m, 14H, $-(CH_2)_7-$), 1.69 (m, 2H, $-CH_2^b-$), 1.86 (m, 2H, $-CH_2^a-$), 3.41 (t, 2H, $-CH_2Br$). 4.15 (t, 2H, $-COOCH_2$), 5.79–6.44 (m, 3H, $CH_2{=}CH-$)
11-Bromoundecylmethacrylate	δ 1.29 (m, 14H, $-(CH_2)_7-$, 1.54 (m, 2H, $-CH_2^b$), 1.72 (m, 2H, $-CH_2^a-$), 3.46 (t, 2H, $-CH_2Br$), 1.98 (s, 3H, CH_3-), 4.11 (t, 2H, $-COOCH_2$), 5.55, 6.10 (2d, 2H, $CH_2{=}C\!<$)
6-Bromohexanylacrylate	δ 1.29 (m, 4H, $-(CH_2)_2-$), 1.67 (m, 2H, $-CH_2^b-$), 1.86 (m, 2H, $-CH_2^a-$), 3.41 (t, 2H, $-CH_2Br$), 4.15 (t, 2H, $-COOCH_2$), 5.80–6.44 (m, 3H, $CH_2{=}CH-$)
6-Bromohexanylmethacrylate	δ 1.24 (m, 4H, $-(CH_2)_2-$), 1.62 (m, 2H, $-CH_2^b-$), 1.83 (m, 2H, $-CH_2^a-$), 2.01 (s, 3H, CH_3-), 3.44 (t, 2H, $-CH_2Br$), 4.14 (t, 2H, $-COOCH_2$), 5.54, 6.11 (2d, 2H, $CH_2{=}C\!<$)



(2)



(3)

Synthesis of polymerizable and non-polymerizable diquaternary ammonium bromides PDQI-VI and DQI-V

These were prepared according to equation (3).

Typically PMQI (5.5 g, 0.012 mol) was dissolved in analytical grade acetone (10 ml) (methanol (20 ml) in the case of preparing DQI-V) in a round-bottomed flask fitted with a drying tube. While stirring, the solution was cooled in ice for 15 min. An excess of cooled bromomethane (3.24 g, 0.034 mol) in diethyl ether (18 ml) was then added and the solution was left stirring for 2 days. A white precipitate appeared after addition of ether. The precipitate was filtered and washed with ether. The white solid was then reprecipitated from methanol solution by addition of ether. The weight of product obtained was 3.2 g (49%).

Experimental data for the other diquaternary salts are shown in *Table 6*, while *Table 7* contains the elemental microanalytical data. *Table 8* summarizes the ^1H n.m.r. assignments (see *Scheme 2* for structures).

Melting points and solubility

In contrast to PMQI-VI, all the diquaternary ammonium salts were crystalline materials whose melting points could be determined in the usual way (Gallenkamp Digital Melting Point Apparatus). The data is shown in *Table 9* along with the monoquaternary

Table 3 Preparation of polymerizable and non-polymerizable monoquaternary ammonium bromides

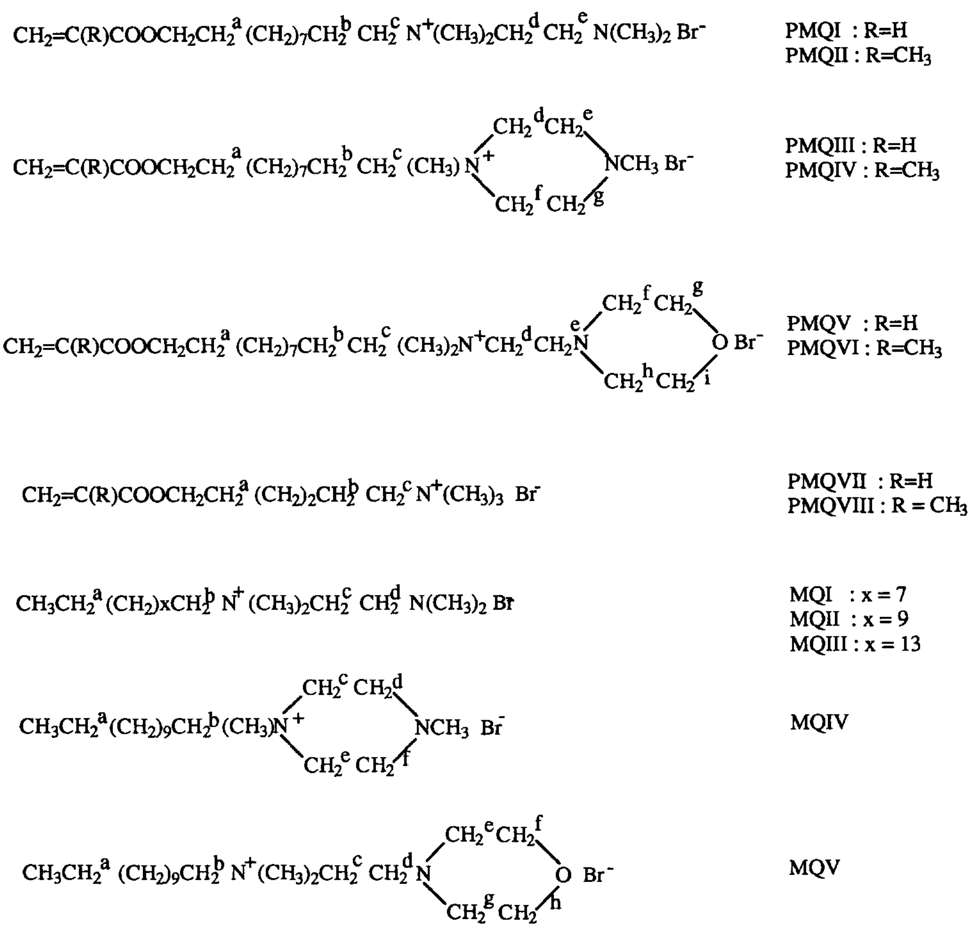
Product	Amine (g, mol)	Bromide (g, mol)	Product (g)	Yield (%)
PMQI	10.0, 9.0×10^{-2}	5.9, 2.0×10^{-2}	6.3	78
PMQII	10.3, 9.0×10^{-2}	6.8, 2.0×10^{-2}	6.6	72
PMQIII	12.1, 1.0×10^{-1}	8.5, 3.0×10^{-2}	5.4	47
PMQIV	8.2, 7.0×10^{-2}	5.5, 2.0×10^{-2}	5.2	69
PDQV	11.4, 7.0×10^{-2}	5.4, 2.0×10^{-2}	5.7	70
PDQVI	7.0, 4.0×10^{-2}	3.7, 1.0×10^{-2}	3.5	64
PDQVII	3.0, 5.0×10^{-2}	1.8, 7.2×10^{-3}	2.0	95
PMQVIII	2.3, 5.0×10^{-2}	2.3, 9.5×10^{-3}	1.9	65
MQI	21.2, 1.8×10^{-1}	10.1, 5.0×10^{-2}	6.3	41
MQII	18.0, 1.5×10^{-1}	10.0, 4.0×10^{-2}	11.0	75
MQIII	13.9, 1.2×10^{-1}	9.8, 4.0×10^{-2}	6.2	46
MQIV	18.3, 1.6×10^{-1}	10.4, 4.0×10^{-2}	11.0	69
MQV	26.7, 1.6×10^{-1}	10.5, 4.0×10^{-2}	13.3	78

Table 4 Elemental microanalytical data for the polymerizable and non-polymerizable monoquaternary ammonium bromides

	Microanalytical data (%)							
	Calculated				Found			
Compound	C	H	N	Br	C	H	N	Br
PMQI	57.0	9.8	6.7	19.0	56.7	10.4	5.7	19.3
PMQII	57.9	10.0	6.4	18.3	56.9	10.6	6.2	17.9
PMQIII	57.3	9.4	6.7	19.0	56.0	9.9	6.9	18.9
PMQIV	58.2	9.5	6.5	18.4	57.4	9.5	6.1	17.9
PMQV	57.0	9.4	6.0	17.3	56.5	9.6	6.1	17.5
PMQVI	57.9	9.5	5.9	16.7	56.3	9.3	6.0	17.1
PMQVII	49.0	8.2	4.5	27.2	47.2	8.5	4.5	28.3
PMQVII	50.7	8.5	4.5	25.9	50.4	8.8	4.4	26.2
MQI	57.0	11.1	8.3	23.7	56.2	11.6	8.0	24.3
MQII	59.2	11.3	7.7	21.9	58.0	11.3	7.6	23.1
MQIII	62.7	11.7	6.7	19.0	62.6	12.2	6.5	18.8
MQIV	59.5	10.8	7.7	22.0	59.0	10.5	6.9	19.6
MQV	59.0	10.6	6.9	19.6	58.7	11.2	8.0	22.1

Table 5 ^1H n.m.r. assignments for polymerizable and non-polymerizable monoquaternary ammonium bromides (see structures in *Scheme 1*)

Compound	^1H n.m.r. resonances in CD_3OD (250 MHz): δ (ppm)
PMQI	1.27 (m, 14H, $-(CH_2)_7-$), 1.64 (m, 2H, $-CH_2^a-$), 1.70 (m, 2H, $-CH_2^b-$), 2.30 (s, 6H, $-N(CH_3)_2$), 2.76 (t, 2H, $-CH_2^eN$), 3.17 (s, 6H, $-N^+(CH_3)_2-$), 3.30 (t, 2H, $-CH_2^cN^+$), 3.43 (t, 2H, $-N^+CH_2^d$), 4.15 (t, 2H, $-COOCH_2-$), 5.86–6.41 (m, 3H, $CH_2{=}CH-$)
PMQII	1.21 (m, 14H, $-(CH_2)_7-$), 1.66 (m, 2H, $-CH_2^a-$), 1.71 (m, 2H, $-CH_2^b-$), 1.84 (s, 3H, $=C(CH_3)-$), 2.32 (s, 6H, $-N(CH_3)_2$), 2.73 (t, 2H, $-CH_2^eN$), 3.16 (s, 6H, $-N^+(CH_3)_2-$), 3.39 (t, 2H, $-CH_2^cN^+$), 3.50 (t, 2H, $-N^+CH_2^d$), 4.14 (t, 2H, $-COOCH_2-$), 5.62, 6.07 (m, 2H, $CH_2{=}C$)
PMQIII	1.34 (m, 14H, $-(CH_2)_7-$), 1.64 (m, 2H, $-CH_2^a-$), 1.80 (m, 2H, $-CH_2^b-$), 2.40 (s, 3H, NCH_3), 2.77 (t, 4H, $CH_2^{e,g}N$), 3.13 (s, 3H, N^+CH_3), 3.39 (t, 2H, $-CH_2^cN^+$), 3.46 (t, 4H, $NCH_2^{d,f}$), 4.15 (t, 2H, $-COOCH_2-$), 5.87–6.41 (m, 3H, $CH_2{=}CH-$)
PMQIV	1.20 (m, 14H, $-(CH_2)_7-$), 1.57 (m, 2H, $-CH_2^a$), 1.70 (m, 2H, $-CH_2^b-$), 1.86 (s, 3H, $=C(CH_3)-$), 2.34 (s, 3H, NCH_3), 2.73 (t, 4H, $CH_2^{e,g}N$), 3.14 (s, 4H, N^+CH_3), 3.40 (t, 2H, CH_2N^+), 3.48 (t, 4H, $N^+CH_2^{d,f}$), 4.15 (t, 2H $-COOCH_2-$), 5.47, 6.02 (2d, 2H, $CH_2{=}C$)
PMQV	1.35 (m, 14H, $-(CH_2)_7-$), 1.65 (m, 2H, $-CH_2^a-$), 1.70 (m, 2H, $-CH_2^b-$), 2.47 (m, (unresolved), 8H, $NCH_2^{f,g,h,i}$), 2.78 (5, 2H, CH_2^eN), 3.18 (s, 6H, $N^+(CH_3)_2$), 3.40 (t, 2H, $N^+CH_2^d$), 3.67 (t, 2H, CH_2^cN), 4.15 (t, 2H, $-COOCH_2-$), 5.86–6.41 (m, 3H, $CH_2{=}CH-$)
PMQVI	1.30 (m, 14H, $-(CH_4)_7-$), 1.66 (m, 2H, $-CH_2^a-$), 1.70 (m, 2H, $-CH_2^b-$), 1.81 (s, 3H, $=C(CH_3)-$), 2.50 (m, 8H, $NCH_2^{f,g,h,i}$), 2.74 (t, 2H, CH_2^eN), 3.35 (s, 6H, $N^+(CH_3)_2$), 3.45 (t, 2H, $CH_2^cN^+$), 3.68 (t, 2H, $N^+CH_2^d$), 4.14 (t, 2H, $-COOCH_2-$), 5.61, 6.07 (2d, 2H, $CH_2{=}C$)
PMQVII	1.37 (m, 4H, $-(CH_2)_2-$), 1.56 (m, 2H, $-CH_2^a-$), 1.73 (m, 2H, $-CH_2^b-$), 3.14 (s, 9H, $-N^+(CH_3)_3$), 3.30 (t, 2H, $CH_2^cN^+$), 4.15 (t, 2H, $-COOCH_2-$), 5.86–6.42 (m, 3H, $CH_2{=}CH-$)
PMQVIII	1.35 (m, 4H, $-(CH_2)_2-$), 1.65 (m, 2H, $-CH_2^a-$), 1.74 (m, 2H, $-CH_2^b-$), 1.93 (s, 3H, CH_3-), 3.14 (s, 9H, $-N^+(CH_3)_3$), 3.36 (t, 2H, $CH_2^cN^+$), 4.15 (t, 2H, $-COOCH_2$), 5.61–6.08 (2d, 2H, $CH_2{=}C$)
MQI	0.90 (t, 3H, $-CH_3$), 1.27 (m, 14H, $-(CH_2)_7$), 1.78 (m, 2H, $-CH_2^a-$), 2.31 (s, 6H, $N(CH_3)_2$), 2.76 (t, 2H, CH_2^dN), 3.17 (s, 6H, $N^+(CH_3)_2$), 3.22 (t, 2H, $CH_2^bN^+$), 3.44 (t, 2H, $N^+CH_2^c$)
MQII	0.73 (t, 3H, $-CH_3$), 1.12 (m, 18H, $-(CH_2)_9-$), 1.59 (m, 2H, $-CH_2^a-$), 2.16 (s, 6H, $N(CH_3)_2$), 3.26 (s, 6H, $N^+(CH_3)_2$), 2.69 (t, 2H, CH_2^dN), 3.39 (t, 2H, $N^+CH_2^c$), 3.53 (t, 2H, $CH_2^bN^+$)
MQIII	0.90 (t, 3H, $-CH_3$), 1.29 (m, 26H, $-(CH_2)_{13}-$), 1.77 (m, 2H, $-CH_2^a-$), 2.30 (s, 6H, $N(CH_3)_2$), 2.75 (t, 2H, CH_2^dN), 3.15 (s, 6H, $N^+(CH_3)_2$), 3.32 (t, 2H, $CH_2^bN^+$), 3.54 (t, 4H, $N^+CH_2^c$)
MQIV	0.82 (t, 3H, $-CH_3$), 1.87 (m, 18H, $-(CH_2)_9-$), 1.91 (m, 2H, $-CH_2^a-$), 2.34 (s, 3H, NCH_3), 2.77 (t, 4H, $CH_2^{d,f}N$), 3.35 (s, 3H, N^+CH_3), 3.56 (t, 2H, $CH_2^bN^+$), 3.77 (t, 4H, $N^+CH_2^{c,e}$)
MQV	0.90 (t, 3H, $-CH_3$), 1.30 (m, 18H, $-(CH_2)_9-$), 1.78 (m, 2H, $-CH_2^a-$), 2.52 (s, 8H, $NCH_2^{e,f,g,h}$), 2.80 (t, 2H, CH_2^dN), 3.18 (s, 6H, $N^+(CH_3)_2$), 3.40 (t, 2H, $N^+CH_3^c$), 3.50 (t, 2H, $CH_2^bN^+$)



Scheme 1 Monovalent surfactants

ammonium species which exhibited sharp melting transitions.

Solubilities of all the surfactants synthesized were assessed visually in solvents of a wide range of polarity, ethanol to hexane. The results are shown in *Table 10*.

Homopolymerization of selected polymerizable surfactants

Representative examples of the various polymerizable mono- and divalent quaternary ammonium ion surfactants were selected to evaluate their homopolymerizability. These experiments were also to provide samples of such homopolymers for comparison of their surface activity properties with those of their corresponding monomers. Polymerizations were carried out using both thermal and photochemical free radical initiators typically as follows. No attempt was made to exclude O_2 from these reactions.

Photo-initiation

PMQ-VIII (5.02 g, 0.02 mol) was placed in a round-bottomed flask along with 2,2-dimethoxy-2-phenyl acetophenone (DMPAP) (0.5 g) and water (40 ml). The flask was shaken thoroughly until the monomer was

Table 6 Preparation of the polymerizable and non-polymerizable diquaternary ammonium bromides

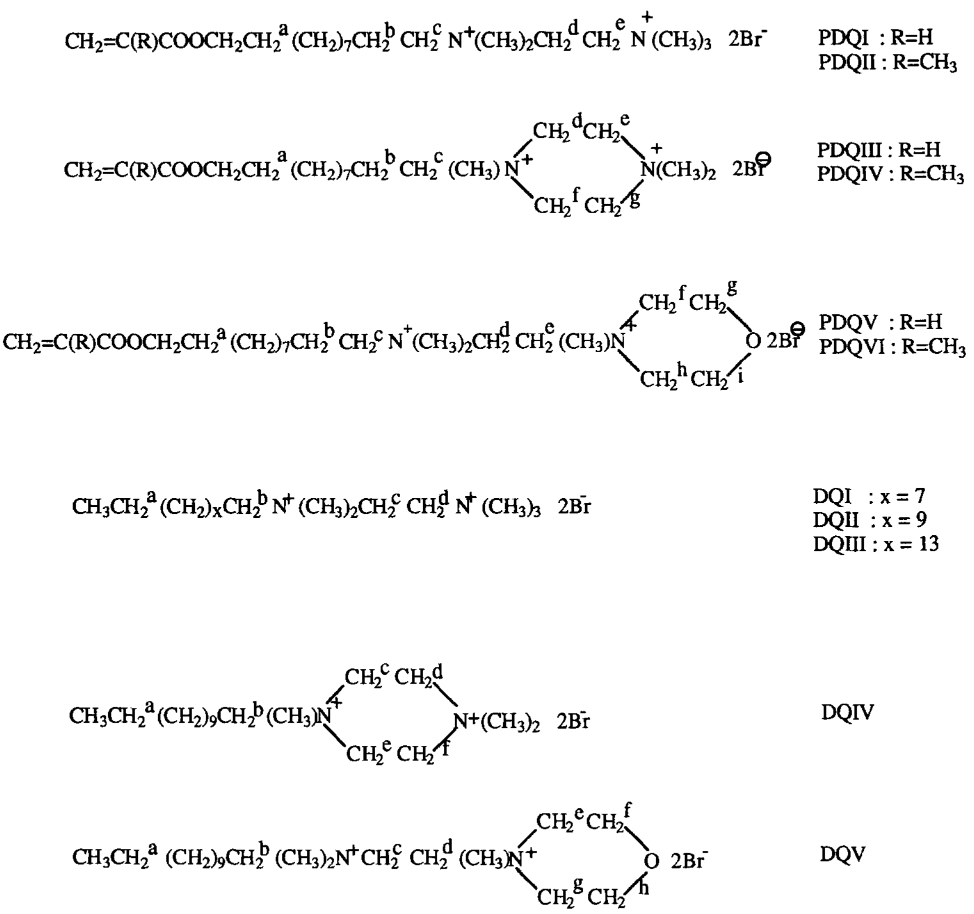
Product	Monoquaternary ammonium bromide (g, mol)	Methyl bromide (g, mol)	Product (g)	Yield (%)
PDQI	5.5, 1.2×10^{-2}	3.2, 3.4×10^{-2}	3.2	49
PDQII	6.0, 1.3×10^{-2}	3.8, 4.0×10^{-2}	4.4	60
PDQIII	6.2, 1.5×10^{-2}	4.5, 5.0×10^{-2}	4.0	53
PDQIV	5.4, 1.2×10^{-2}	3.4, 4.0×10^{-2}	3.2	49
PDQV	5.9, 1.3×10^{-2}	3.9, 4.0×10^{-2}	3.6	51
PDWVI	6.7, 1.4×10^{-2}	4.1, 4.0×10^{-2}	4.5	57
DQI	5.1, 1.5×10^{-2}	4.3, 5.0×10^{-2}	4.2	64
DQII	6.0, 1.6×10^{-2}	4.7, 5.0×10^{-2}	3.7	49
DQIII	4.2, 1.0×10^{-2}	3.2, 3.0×10^{-2}	4.4	85
DQIV	5.1, 1.4×10^{-2}	4.0, 4.0×10^{-2}	3.7	58
DQV	3.2, 8.0×10^{-3}	2.5, 3.0×10^{-2}	1.5	38

Table 7 Elemental microanalytical data for the polymerizable and non-polymerizable diquaternary ammonium bromides

	Microanalytical data (%)							
	Calculated				Found			
Compound	C	H	N	Br	C	H	N	Br
PDQI	48.8	8.6	5.4	31.0	46.6	8.8	5.4	30.3
PDQII	49.8	8.7	5.1	30.1	49.0	8.8	5.1	30.3
PDQIII	49.0	8.2	5.5	31.1	48.4	8.6	5.4	32.3
PDQIV	50.0	8.4	5.3	30.4	49.0	8.4	5.0	31.1
PDQV	49.5	8.3	5.0	28.6	48.6	8.6	5.2	29.6
PDQVI	51.8	8.7	5.0	28.7	48.6	8.8	5.0	29.0
DQI	47.2	9.3	6.5	37.0	47.2	9.3	6.5	37.0
DQII	49.6	9.6	6.1	34.8	48.8	9.6	6.0	35.6
DQIII	53.5	10.2	5.4	30.9	53.0	10.2	5.3	31.4
DQIV	49.8	9.2	6.1	34.9	49.9	9.4	6.2	34.3
DQV	50.2	9.2	5.6	31.8	49.1	9.0	5.7	31.3

Table 8 ^{1}H n.m.r. assignments for polymerizable and non-polymerizable diquaternary ammonium bromides (see structures in *Scheme 2*)

Compound	^{1}H n.m.r. resonances in D_2O (250 MHz): δ (ppm)
PDQI (400 MHz Cosy)	1.56 (m, 16H, $-(CH_2)_7-$), 1.90 (m, 2H, $-CH_2^a-$), 2.05 (m, 2H, $-CH_2^b-$), 3.43 (s, 6H, $-N^+(CH_3)_2$), 3.51 (s, 9H, $-N^+(CH_3)_3$), 3.66 (t, 2H, $CH_2^cN^+$), 4.16 (s, 2H, $N^+CH_2^e$), 4.19 (s, 2H, $CH_2^dN^+$), 4.40 (t, 2H, $-COOCH_2-$), 6.18–6.64 (m, 3H, $CH_2{=}CH$)
PDQII	1.28 (m, 14H, $-(CH_2)_7-$), 1.47 (m, 2H, $-CH_2^a-$), 1.65 (m, 2H, $-CH_2^b-$), 1.82 (s, 3H, $=C(CH_3)-$), 3.21 (s, 6H, $-N^+(CH_3)_2$), 3.32 (s, 6H, $-N^+(CH_3)_3$), 3.52 (t, 2H, $CH_2^cN^+$), 4.09 (s (unresolved), 4H, $N^+CH_2^{d,e}$), 4.12 (t, 2H, $-COOCH_2-$), 5.64, 6.07 (2d, 2H, $CH_2{=}C$)
PDQIII	1.32 (m, 16H, $-(CH_2)_8-$), 1.58 (m, 2H, $-CH_2^a-$), 1.68 (m, 2H, $-CH_2^b-$), 3.40 (s, 3H, N^+CH_3), 3.49 (s, 6H, $N^+(CH_3)_2$), 3.86 (t, 2H, $CH_2^cN^+$), 4.05 (s (unresolved), 8H, $N^+CH_2^{d,e,f,g}$), 4.14 (t, 2H, $-COOCH_2-$), 5.95–6.50 (m, 3H, $CH_2{=}CH$)
PDQIV	1.36 (m, 14H, $-(CH_2)_7-$), 1.48 (m, 2H, $-CH_2^a-$), 1.68 (m, 2H, $-CH_2^b-$), 1.93 (s, 3H, $=C(CH_3)-$), 3.38 (s, 3H, N^+CH_3), 3.48 (s, 6H, $N^+(CH_3)_2$), 3.70 (t, 2H, $CH_2^cN^+$), 4.14 (t, 2H, $-COOCH_2-$), 4.02 (s (unresolved), 8H, $N^+CH_2^{d,e,f,g}$), 5.06, 6.08 (2d, 2H, $CH_2{=}C$)
PDQV	1.35 (m, 14H, $-(CH_2)_7-$), 1.65 (m, 2H, $-CH_2^a-$), 1.86 (m, 2H, $-CH_2^b-$), 3.24 (s, 6H, $N^+(CH_3)_2$, 3.52 (t, 2H, $N^+CH_2^d$), 3.43 (s, 3H, N^+CH_3), 3.73 (s (unresolved), 8H, $N^+CH_2^{f,g,h,i}$), 4.07 (s (unresolved), 4H, $N^+CH_2^{d,e}$), 4.17 (t, 2H, $-COOCH_2-$), 5.86–6.41 (m, 3H, $CH_2{=}CH-$)
PDQVI	1.28 (m, 14H, $-(CH_2)_7-$), 1.65 (m, 2H, $-CH_2^a-$), 1.70 (m, 2H, $-CH_2^b-$), 1.90 (s, 3H, $=C(CH_3)-$), 3.21 (s, 6H, $N^+(CH_3)_2$), 3.42 (t, 2H, $CH_2^cN^+$), 3.34 (s, 3H, N^+CH_3), 3.59 (s (unresolved), 8H, $N^+CH_2^{f,g,h,i}$), 4.06 (s (unresolved), 4H, $N^+CH_2^{d,e}$), 4.19 (t, 2H, $-COOCH_2-$), 5.67, 6.09 (2d, 2H, $CH_2{=}C$)
DQI	0.85 (t, 3H, CH_3-), 1.29 (m, 16H, $-(CH_2)_8-$), 1.83 (m, 2H, $-CH_2^a-$), 3.25 (s, 6H, $N^+(CH_3)_2$), 3.32 (s, 9H, $-N^+(CH_3)_3$), 3.50 (t, 2H, $CH_2^bN^+$), 4.01 (s (unresolved), 4H, $N^+CH_2^{c,d}$)
DQII	0.89 (t, 3H, CH_3-), 1.29 (m, 18H, $-(CH_2)_9-$), 1.86 (m, 2H, $-CH_2^a-$), 3.28 (s, 6H, $N^+(CH_3)_2$), 3.36 (s, 9H, $-N^+(CH_3)_3$), 3.52 (t, 2H, $CH_2^bN^+$), 4.10 (s, 2H, $N^+CH_2^c$), 4.16 (s, 2H, $CH_2^dN^+$)
DQIII	0.90 (t, 3H, $-CH_3$), 1.29 (m, 26H, $-(CH_2)_{13}-$), 1.89 (m, 2H, $-CH_2^a-$), 3.28 (s, 6H, $N^-(CH_3)_2$), 3.35 (s, 9H, $N^+(CH_3)_3$), 3.50 (t, 2H, $CH_2^bN^+$), 4.09 (s, 2H, $N^+CH_2^c$), 4.13, (s, 2H, $CH_2^dN^-$)
DQIV	0.88 (t, 3H, $-CH_3-$), 1.32 (m, 18H, $-(CH_2)_9-$), 1.89 (m, 2H, $-CH_2^a-$), 3.31 (s, 3H, $N^+(CH_3)_2$), 3.60 (t, 2H, $CH_2^bN^+$), 3.37 (s, 6H, $N^+(CH_3)_2$), 4.14 (s (unresolved), 8H, $N^+CH_2^{c,d,e,f}$)
DQV	0.86 (t, 3H, CH_3), 1.22 (m, 18H, $-(CH_2)_9-$), 1.85 (m, 2H, $-CH_2^a-$), 3.28 (s, 6H, $N^+(CH_3)_2$), 3.40 (s, 3H, N^-CH_3), 3.56 (t, 2H, $CH_2^bN^+$), 3.71 (s (unresolved), 4H, $N^+CH_2^{c,d}$), 4.07 (s (unresolved), 8H, $N^+CH_2^{e,f,g,h}$)



Scheme 2 Divalent surfactants

dissolved and the initiator was solubilized. The flask was then irradiated with u.v. light (Rayonet Type R5) for 24 h. The solution became viscous and remained clear. Water was then removed by freeze drying to yield a white solid. The solid was washed in chloroform to remove any residual initiator and monomer. After filtering and drying the weight of product was 4.13 g (82%).

Thermal initiation

PMQ-III (3.24 g, 7.72×10^{-3} mol) was placed in a round-bottomed flask along with azobisisobutyronitrile (AIBN) (0.03 g) and water (40 ml). After shaking the flask vigorously it was stirred for a further 10 min. While continuing to stir, the flask and its contents were placed in an oil bath and heated at 80°C for 24 h. After cooling the contents were freeze dried and washed with acetone to remove residual initiator and monomer. The weight of product obtained was 3.16 g (98%).

Table 9 Melting points for all surfactants obtained as crystalline solids

Divalent surfactant	Melting point (°C)	Monovalent surfactant	Melting point (°C)
PDQI	70–71	—	—
PDQII	166–168	—	—
PDQIII	280–282	—	—
PDQIV	267–268	—	—
PDQV	222–223	PMQVII	130–131
PDQVI	212–214	PMQVIII	Gels at 145
DQI	187–188	—	—
DQII	198–199	MQII	110–111
DQIII	239–240	MQIII	90–92
DQIV	285–286 (dec.)	MQIV	254–255
DQV	226–228	MQV	120–121

A summary of the results of all the homopolymerizations carried out is given in *Table 11*, while the solubilities of the polymers produced are indicated in *Table 12*.

RESULTS AND DISCUSSION

Syntheses of monomers

Synthesis of polymerizable surfactants can be hampered by two main problems: the surface active nature of intermediate products, leading to difficulties with isolation and purification, and spurious polymerization of the double bond. To overcome these problems it is usual to generate the ionic group and introduce the double bond as late as possible in the reaction sequence. Also, it is important to employ mild reaction conditions and use polymerization inhibitors in order to prevent spurious polymerization.

The strategy used in the present work was to synthesize appropriate long chain ω-bromoalkanyl(meth)acrylates [equation (1)] and then to employ these in alkylating appropriate tertiary amines [equation (2)] to yield, initially, monoquaternary ammonium bromides. The ω-bromoalkanyl(meth)acrylates were obtained in good yields (*Table 1*) and reasonable purity, as indicated by elemental microanalyses (*Table 1*) and ^{1}H n.m.r. spectra (*Table 2*).

Table 10 Solubility data for all monomeric surfactants

	Solvent											
	Ethanol		Acetone		Chloroform		Ethyl acetate		Diethyl ether		Hexane	
Surfactant	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)
PMQI	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
PMQII	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
PMQIII	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
PMQIV	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
PMQV	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
PMQVI	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
PMQVII	+ + +	+ + +	+	+ + +	+ + +	+ + +	x	x	x	x	x	x
PMQVIII	+ + +	+ + +	x	x	+ + +	+ + +	x	x	x	x	x	x
MQI	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
MQII	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
MQIII	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
MQIV	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
MQV	+ + +	+ + +	+ + +	+ + +	+ + +	+ + +	+	+ + +	x	x	x	x
PDQI	+ + +	+ + +	x	x	+ + +	+ + +	x	x	x	x	x	x
PDQII	+ + +	+ + +	x	x	+ + +	+ + +	x	x	x	x	x	x
PDQIII	+ + +	+ + +	x	x	x	x	x	x	x	x	x	x
PDQIV	+ + +	+ + +	x	x	x	x	x	x	x	x	x	x
PDQV	+ + +	+ + +	x	x	x	x	x	x	x	x	x	x
PDQVI	+ + +	+ + +	x	x	x	x	x	x	x	x	x	x
DQI	+ + +	+ + +	x	x	+ + +	+ + +	x	x	x	x	x	x
DQII	+ + +	+ + +	x	x	x	x	x	x	x	x	x	x
DQIII	+ + +	+ + +	x	x	+ + +	+ + +	x	x	x	x	x	x
DQIV	+ + +	+ + +	x	x	x	x	x	x	x	x	x	x
DQV	+ + +	+ + +	x	x	x	x	x	x	x	x	x	x

All are soluble in water and methanol. Key: + (slightly soluble); + + + (very soluble); x (insoluble); C (cold); H (hot)

Monoalkylation of the diamines, tetramethylethylene diamine, 1,4-dimethylpiperazine and 4-[2-(dimethylamino)-ethyl]morpholine to yield the monovalent surfactants PMQI-VI was achieved more easily than originally anticipated. In each case the diamine was used in excess in the synthesis and any dialkylated product was readily separated, because the diquaternary ammonium species, e.g. $[CH_2CHCO_2(CH_2)_{11}N^+(CH_3)_2CH_2]_2$ is insoluble in alcohols and ethyl acetate. The yields of the monovalent surfactants were as a result generally quite good (*Table 3*). Compounds PMQI-VI and MQI proved to be rather deliquescent and no satisfactory melting points could be obtained. This is in contrast to the range of polymerizable trimethylammonium surfactant salts prepared previously[1] which showed exemplary melting behaviour. Despite this, however, the analytical data on all the monovalent surfactants was satisfactory (*Tables 4* and *5*) and the structural assignments (*Scheme 1*) were justified.

Table 11 Homopolymerizations of representative polymerizable mono- and divalent surfactants

Monomer	Monomer (g, mol)	Initiator (g)	Water (ml)	Yield of polymer (%)
PMQIII	$3.0, 7.3 \times 10^{-3}$	0.03^a	40	90
PMQV	$6.0, 1.2 \times 10^{-2}$	0.06^a	40	96
PMQVII	$2.0, 6.8 \times 10^{-3}$	0.02^a	40	95
PMQVIII	$5.0, 1.6 \times 10^{-2}$	0.05^a	40	82
PDQI	$5.0, 9.8 \times 10^{-3}$	0.05^a	40	95
PDQII	$3.0, 6.0 \times 10^{-3}$	0.03^a	40	99
PDQIII	$3.0, 5.6 \times 10^{-3}$	0.03^a	40	94
PMQIII	$3.0, 7.7 \times 10^{-3}$	0.03^b	40	98
PMQV	$5.0, 1.1 \times 10^{-2}$	0.05^b	40	89
PMQVII	$5.0, 1.7 \times 10^{-2}$	0.05^b	40	90
PMQVIII	$5.0, 1.4 \times 10^{-2}$	0.04^b	40	93
PMQI	$5.0, 9.5 \times 10^{-3}$	0.05^b	40	96
PDQII	$3.0, 5.6 \times 10^{-3}$	0.03^b	40	98
PDQIII	$3.0, 5.9 \times 10^{-3}$	0.03^b	40	88

[a] Photochemical initiation using DMPAP
[b] Thermal initiation using AIBN

The divalent quaternary ammonium surfactant salts, PDQI-VI and DQI-V, were prepared by methylation of each corresponding monoquaternary ammonium salt [equation (3)] using methyl bromide. While there is precedence for related species in the literature[13], to our knowledge no polymerizable analogues have been reported before. The yields in the final methylation step were reasonable (*Table 6*) and the crystalline structure of these diquaternary ammonium species enabled good purity to be attained on reprecipitation, indicated by the elemental microanalytical data (*Table 7*). None of these species displayed the problem of the deliquescence shown by some of the monovalent salts. In all cases the ^1H n.m.r. spectral analysis was consistent with the proposed structures (*Table 8*). PDQI was also analysed by the COST technique (400 MHz) to confirm the chemical shift assignment.

An interesting feature detected in the ^1H n.m.r. spectra of these surfactants is a notable change in chemical shift and a broadening of the peaks associated with protons in

Table 12 Solubility data for representative polymeric surfactants

	Solvent													
	Water		Methanol		Ethanol		Acetone		Chloroform		Ethyl acetate		Diethyl ether	
Polymeric surfactant	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)	(C)	(H)
Poly PMQI	+++	+++	x	x	x	x	x	x	x	++	x	x	x	x
Poly PMQIII	+++	+++	x	x	x	x	x	x	x	++	x	x	x	x
Poly PMQV	+++	+++	x	x	x	x	x	x	x	++	x	x	x	x
Poly PMQVII	+++	+++	x	x	x	x	x	x	x	x	x	x	x	x
Poly PMQVIII	+++	+++	x	x	x	x	x	x	x	x	x	x	x	x
Poly PDQI	+++	+++	x	x	x	x	x	x	x	x	x	x	x	x
Poly PDQII	+++	+++	x	x	x	x	x	x	x	x	x	x	x	x
Poly PDQIII														

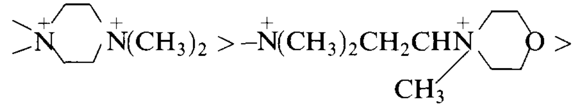
Key: ++ (slightly soluble); + + + (very soluble); x (insoluble); C (cold); H (hot)

the polar part of the molecule, when chloroform is used as a solvent instead of methanol or water. It is known that some similar surfactants are able to form reverse micelles in organic solvents[14]. If this is indeed happening with our surfactants then the change in chemical shift could well be due to the polar regions of the surfactant being located in the centre of the reverse micelle, instead of being found at the surface of the normal micelle in water or methanol. Thus, the chemical shift (400 MHz) for $R_3N^+\underline{CH_2}\underline{CH_2}N^+R_3$ is typically 4.17–4.19 in D_2O and 4.61–4.69 in $CDCl_3$.

Solubility and melting characteristics

Compounds having an amphiphilic nature are usually able to dissolve in a variety of solvents typically ranging from water to chloroform. This was the case with the monoquaternary ammonium salts prepared here (*Table 10*). Only diethyl ether and hexane proved to be non-solvents for these species. PMQ-VII and VIII differed from the rest in showing poor or lack of solubility also in acetone and ethyl acetate. This was, however, consistent with the structures of these two molecules which have much shorter hydrocarbon tails and are, in effect, significantly more hydrophilic than the rest (see Paper II). In this respect these molecules are similar to the diquaternary ammonium amphiphiles PDQI-VI and DQI-V prepared in this work. These species have two ionic groups associated with the same organic frameworks as the monoquaternary salts, and so not surprisingly in general proved to be soluble only in the polar protic solvents: water, methanol and ethanol. However, PDQI, PDQII, DQI and DQIII were also soluble in chloroform. This was a little surprising since the hydrocarbon content of PDQIII-VI and DQIV and V is a little higher. The headgroups of the latter molecules are, however, probably more rigid and hence, the interactions in the crystalline state possibly a little stronger. PDQI, PDQII and DQI do indeed have the lowest melting points of the diquaternary ammonium ion species, although DQIII appears to be anomalous in this respect (*Table 9*).

The monovalent species PMQI-IV and MQI were too deliquescent to display sharp melting points. In general, however, the melting points of the divalent species are consistently higher than the monovalent species from which each was derived and this is consistent with the greater ionic nature of these species (*Table 9*). A trend in the melting point is also noted with a change in the structure of the headgroup, increasing in the order:



$-\overset{+}{N}(CH_3)_2CH_2CH_2\overset{+}{N}(CH_2)_2$

The relative magnitude of these melting points is the same in both the acrylate and methacrylate series of polymerizable diquaternary ammonium species and also in the non-polymerizable model compounds. This presumably therefore reflects the same relative crystal packing and solid state interaction parameters in these three series of structurally analogous molecules. Finally, for a given surfactant structure the melting point is seen to rise with an increase in the chain length of the hydrophobic hydrocarbon tail (DQI-III). This effect has been well reported before (ref. 1 and references therein).

Homopolymerization of polymerizable surfactants

In principle homopolymerization of the (meth)acrylate surfactants in this work might yield analogous polysurfactants or polymer surfactants. These could be of interest by virtue of forming unimolecular 'polymerized micelles' at all finite concentrations, i.e. by *not* exhibiting critical micelle concentration behaviour. Such polysurfactants might also adsorb strongly at surfaces and interfaces *and desorb very slowly*, in contrast to monomeric or low molecular weight surface active molecules.

All the monomers studied in this work (PMQIII-VIII, PDQI-III) polymerized readily and to high conversion using both photochemical and thermal free radical initiators (*Table 11*). The progress of polymerization was monitored using ^1H n.m.r. spectroscopy. The vinyl resonances ($\delta \sim 6.5$–5.5 ppm) were seen to disappear with concomitant broadening of other resonances. The latter effect suggests the normal decrease in the relaxation time for protons due to the inhibited movement of the polymer chain which is formed. Polymerizations were carried out at concentrations well above the critical micelle concentration of each species (see Paper II). The solutions formed were viscous, particularly those derived from PMQ-VII and VIII, the short chain species. This behaviour suggests that the polymers, not surprisingly, have substantial polyelectrolyte behaviour, presumably with highly expanded random coil structures in solution (see Part II).

The clear aqueous solutions resulting from the polymerizations in this work are in stark contrast to those of our earlier work involving polymerization of long alkyl chain quaternary ammonium derivatives of N,N-dimethylaminoethylmethacrylate[2]. Polymerization of aqueous solutions of the latter produced opaque systems with substantial phase separation of the polymers. The behaviour of the present mono- and diquaternary ammonium (meth)acrylates is very similar to that of the styryl-based monomer systems recently described by Candau and her co-workers[15,16]. The difference in behaviour is difficult to account for and may be associated with the structures of the quaternary ammonium ion centres. However, similar differences in solubility behaviour have been reported previously by Laschewsky and Zerbe[17]. They invoked so-called 'skin-controlled' solubility effects to explain the solubility of polymer surfactants formed from monomers with the headgroup far from the polymerizable group (as in the present work), compared with the poor solubility of polymer surfactants formed from monomers with the headgroup and polymerizable group in close proximity. While this sort of argument seems tenable in the case of dissolving pre-formed polymers from the dry state, it is not clear how significant it is with regard to polymers formed from monomers already fully solvated by solvent (water in this case) molecules.

Freeze drying of the homopolymers formed in this work yielded white amorphous fluffy powders. These proved to re-dissolve with ease in water, and were also readily soluble in methanol (*Table 12*). Viscous solutions resulted even at low concentrations. The polymers from PMQI, PMQIII and PMQV were also reasonably soluble in hot chloroform. While solubilities are likely to be molecular weight dependent, attempts to measure the molecular weights of these polycationic species in methanol using vapour phase osmometry, yielded data which could not be sensibly interpreted. It seems that the aggregation behaviour, viscosity effects and the strong adsorbent nature of these polycationic species preclude this type of physico-chemical evaluation. Light scattering methodologies probably offer better scope[15,16].

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