Preparation, characterization and use in emulsion polymerization of acrylated alkyl ethoxylate surface-active monomers

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A range of commercially available alkyl ethoxylates with different hydrophobes and degrees of ethoxylation have been acrylated to produce structurally analogous polymerizable surfactants. The latter have been polymerized in water using a photochemical free radical initiating system to yield a mixture of linear soluble oligomer and crosslinked polymer. The starting amphiphiles, their acrylate derivatives and their soluble oligomers have been extensively characterized in terms of their molecular structure and their amphiphilic properties. The latter have been discussed in terms of the molecular structure of the series of molecules. Selected examples of the alkyl ethoxylates and their acrylate derivatives have been compared as sole emulsion stabilizers in the polymerization (separately) of styrene, methyl methacrylate and vinyl acetate. In general the conventional surfactants provide better stability, though both an acrylated derivative and its precursor surfactant perform well in styrene polymerizations. The effect of added electrolyte in flocculation studies confirms the superiority of the conventional surfactant. The results are discussed in terms of current colloid and emulsion polymerization theories and practice, and suggestions are made for the improved design of polymerizable amphiphiles.

(Keywords: emulsion; polymerization; acrylate)

INTRODUCTION

Surface-active polymers can be prepared by copolymerization of hydrophilic and hydrophobic monomeric components by appropriate chemical modification of some initially non-surface-active chain or by polymerization of a monomer which is itself surface active. Interest in the latter area focused in the recent past on bilayer-forming monomers[1], but there has existed for some time a growing activity associated with single-chain amphiphilic monomers capable of micellizing, and Paleos and Malliaris[2] reviewed the progress in 1988. Although monomer amphiphiles of the anionic, non-ionic and cationic type have all been described, perhaps the most detailed understanding of the physical organic chemistry of these systems has been provided by cationic systems[3-5]. This has arisen simply because the synthesis of pure samples of a wide range of structural variants is easier with this class of amphiphile. Recently, Laschewsky and Zerbe[6] have reported considerable progress with an interesting range of zwitterionic polymerizable surfactants.

An important group of surface-active non-ionic synthetic polymers are the ethylene oxide/propylene oxide block copolymers. These have been widely researched with the details of some interesting results on their behaviour in water appearing only recently[7].

The chemical modification route to produce non-ionic synthetic polymeric amphiphiles has also been exploited, with a potential application in oil recovery being highlighted[8]. One of the first disclosures of a polymerizable alkyl ethoxylate was by Ito et al.[9] who introduced a dodecyl group onto the free OH of a poly(ethylene oxide) (PEO) monomethacrylate macromer. They employed this amphiphile in dispersion polymerizations in water and hydrocarbon media. Finkelmann's group extended their studies of polysiloxanes with pendant oligo(ethylene oxide) side chains[10] to include polymerizable, non-ionic, amphiphilic monosaccharides[11] and polymerizable acrylated alkyl ethoxylates[12]. The interest here was in the concentrated aqueous lyotropic liquid crystalline phase behaviour of these monomers and their polymers. Use of acrylated, commercially available alkyl ethoxylates was described briefly by Whateley and his co-workers[13,14]. No detailed physical organic studies were carried out since the group was concerned mainly in achieving drug encapsulation by polymerization of these amphiphiles.

Following on from our studies on polymerizable cationic surfactants we now report on the synthesis of some polymerizable non-ionic surfactants derived from readily available commercial materials, on their homopolymerization, their dilute aqueous solution phase behaviour, and their use as emulsifiers in emulsion polymerizations.

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EXPERIMENTAL AND RESULTS

Materials

Acryloyl chloride, lauroyl chloride, myristoyl chloride, palmitoyl chloride and stearoyl chloride were used as supplied by Aldrich Chemical Co. Styrene was obtained from Fisons and was used as supplied. Methyl methacrylate, hydroxyethyl methacrylate and vinyl acetate were supplied by Aldrich Chemical Co. and were washed with dilute sodium hydroxide and water and dried prior to use. Azobisisobutyronitrile (AIBN) was used as supplied by BDH Chemicals Ltd. Quantacure BTC is a water-soluble benzophenone derivative supplied by International Bio-synthetics Ltd. It was used as delivered, as was the coinitiator N,N-dimethylethanolamine from Aldrich Chemical Co. Propanol was supplied by Fisons and toluene by Strathclyde Chemicals. 2-Ethoxyethanol, sodium sulfate, calcium chloride and aluminium chloride hexahydrate were also from Aldrich Chemical Co., whereas sodium chloride and trisodium orthophosphate were from BDH Chemicals Ltd. The water used for surface tension measurements was doubly distilled, while deionized grade was used in polymerization.

Poly(ethylene oxide) monomethacrylate.

This was Blemmer PEO350 supplied by the Nippon Oil and Fats Co. Ltd with the structure $CH_2=C(CH_3)CO(OCH_2CH_2)_yOH$. The PEO350 designation implies an average molecular weight of 350 ($y \sim 8$) for the ethylene oxide (EO) oligomer. The FTi.r. spectrum of this showed all the expected absorbance peaks, and the ^1H n.m.r. 90 MHz ($CDCl_3$) assignments (δ) were as follows: 1.9 (s, 3H, $=CCH_3$); 3.2 (s, 1H, OH); 3.6 (m, 32H, CH_2OCH_2); 4.3 (t, 2H, CO_2CH_2); 5.6–6.1 (m, 2H, $CH_2=C$). In fact, careful analysis of the peaks for the CH_2OCH_2 and $=CCH_3$ protons indicated an average number of EO segments per molecule of 8.4. Blemmer PEO350 is probably therefore a mixture mainly of molecules with eight and nine EO segments, possibly with small amounts of molecules with other EO contents. Elemental microanalysis was as follows: calculated for $C_{21}H_{40}O_{10.5}$, $C = 54.8\%$; $H = 8.8\%$; found, $C = 54.7\%$; $H = 8.7\%$. In syntheses this was used as supplied.

Alkyl ethoxylate surfactants.

These were the commercial Marlipals supplied by Hüls Aktiengesellschaft and possess the generic structure $CH_3(CH_2)_x(OCH_2CH_2)_yOH$. The commercial designations were as follows: 24/120 ($x = 11–13$, $y = 12$); 24/140 ($x = 11–13$, $y = 14$); 24/200 ($x = 11–13$, $y = 20$); 24/300 ($x = 11–13$, $y = 30$); 1618/18 ($x = 15–17$, $y = 18$); 1850/30 ($x = 18$, unsaturated based on oleic, $y = 30$); 1850/40 ($x = 18$, unsaturated based on oleic, $y = 40$). ^1H n.m.r. 90 MHz ($CDCl_3$) assignments are shown in *Table 1*, along with the structure determined by taking the appropriate area ratios of the CH_3, CH_2 and CH_2OCH_2 proton resonances.

Monodisperse alkyl ethoxylate surfactants.

These were research materials obtained from the Nikko Chemical Co. Ltd with nominal structures corresponding to $x = 9$, $y = 8$ and $x = 11$, $y = 8$. The purity was quoted as 99% as analysed by gas–liquid chromatography. Our ^1H n.m.r. analysis is shown in *Table 1*.

Synthesis of alkanoyl PEO monomethacrylates.

These were prepared from a PEO monomethacrylate (Blemmer PEO350) according to equation (1). The method is exemplified with the lauroyl ($x = 10$) derivative. Blemmer PEO350 (8.6 g, 0.02 mol) and pyridine (2 g, 0.02 mol) were dissolved in dichloromethane (dry, 150 ml) and the solution was cooled to 0°C. Lauroyl chloride (6.56 g, 0.03 mol) in dichloromethane (dry, 50 ml) was added dropwise over a period of 45 min. The reaction was allowed to continue for 5 h at 0°C, refluxed for 3 h, and then left overnight at room temperature. The resultant pyridinium salt was filtered off and the solution washed with dilute hydrochloric acid (3×200 ml), saturated sodium bicarbonate (3×200 ml) and finally saturated brine (3×200 ml). A small amount of quinol was added to inhibit polymerization, and the solvent was removed by rotary evaporation to yield the product. Final traces of solvent were removed by connection to a vacuum line overnight (0.3 mmHg). The weight of lauroyl PEO(8–9) methacrylate obtained was 10.4 g, corresponding to a yield of 86.8%.
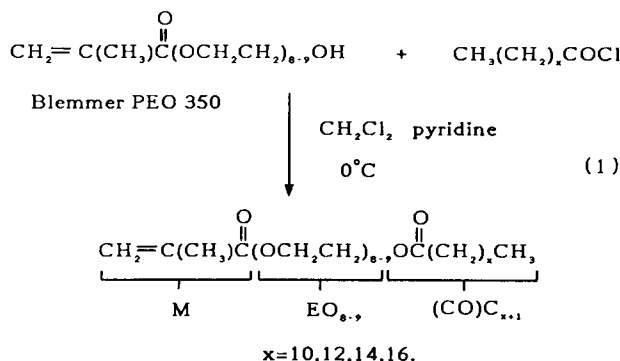
$$CH_2= C(CH_3)\overset{O}{\overset{\|}{C}}(OCH_2CH_2)_{8-9}OH \quad + \quad CH_3(CH_2)_xCOCl$$

Blemmer PEO 350

$$\downarrow \quad CH_2Cl_2 \quad pyridine$$
$$0°C \qquad (1)$$

$$CH_2=C(CH_3)\overset{O}{\overset{\|}{C}}(OCH_2CH_2)_{8-9}O\overset{O}{\overset{\|}{C}}(CH_2)_xCH_3$$

$$\underbrace{\qquad}_{M} \quad \underbrace{\qquad}_{EO_{8-9}} \quad \underbrace{\qquad}_{(CO)C_{x+1}}$$

$$x=10,12,14,16.$$

Table 1 ^1H n.m.r. assignments and structures of alkyl ethoxylate starting materials

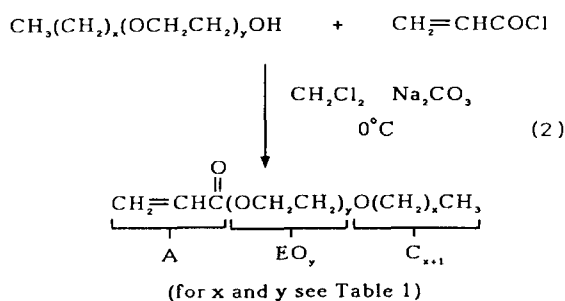| Material	^1H n.m.r. resonances in $CDCl_3$, δ (ppm)	Nominal structure	Determined structure
Marlipal 24/120	0.9 (m, 3H, CH_3), 1.2 (m, 16H, CH_2), 3.6 (m, 36H, CH_2OCH_2)	$EO_{12}C_{12-14}$	$EO_{8.5}C_{10}$
Marlipal 24/140	0.9 (m, 3H, CH_3), 1.2 (m, 20H, CH_2), 3.6 (m, 59H, CH_2OCH_2)	$EO_{14}C_{12-14}$	$EO_{14.5}C_{12}$
Marlipal 24/200	0.9 (m, 3H, CH_3), 1.2 (m, 19H, CH_2), 3.6 (m, 74H, CH_2OCH_2)	$EO_{20}C_{12-14}$	$EO_{18}C_{11.5}$
Marlipal 24/300	0.9 (m, 3H, CH_3), 1.3 (m, 27H, CH_2), 3.6 (m, 181H, CH_2OCH_2)	$EO_{30}C_{12-14}$	$EO_{45}C_{15.5}$
Marlipal 1618/18	0.9 (m, 3H, CH_3), 1.3 (m, 25H, CH_2), 3.6 (m, 68H, CH_2OCH_2)	$EO_{18}C_{16-18}$	$EO_{16.5}C_{14.5}$
Marlipal 1850/30	0.9 (m, 3H, CH_3), 1.3 (m, 24H, CH_2), 3.6 (m, 94H, CH_2OCH_2)	$EO_{30}C_{18}$	$EO_{23}C_{14}$
Marlipal 1850/40	0.9 (m, 3H, CH_3), 1.3 (m, 27H, CH_2), 3.6 (m, 207H, CH_2OCH_2)	$EO_{40}C_{18}$	$EO_{51}C_{15.5}$
Nikko ($x = 9$)	0.9 (t, 3H, CH_3), 1.2 (m, 16H, CH_2), 3.6 (m, 33H, CH_2OCH_2)	EO_8C_{10}	$EO_{7.8}C_{10}$
Nikko ($x = 11$)	0.9 (t, 3H, CH_3), 1.2 (m, 20H, CH_2), 3.6 (m, 33H, CH_2OCH_2)	EO_8C_{12}	$EO_{7.8}C_{12}$

Table 2 ^{1}H n.m.r. assignments and microanalytical data for alkanoyl PEO(8–9) methacrylates

| Compound | ^{1}H n.m.r. resonances in CDCl$_3$, δ (ppm) | Microanalytical data (%) | | | |
| | | Calculated | | Found | |
		C	H	C	H
Lauroyl PEO(8–9) methacrylate ($\text{MEO}_{8-9}(\text{CO})\text{C}_{11}$)	0.9 (m, 3H, CH$_3$), 1.3 (br s, 18H, CH$_2$), 1.9 (m, 3H, =CCH$_3$), 2.3 (t, 2H, CH$_2$COO), 3.7 (m, 30H, CH$_2$OCH$_2$), 4.3 (m, 4H, COOCH$_2$), 5.6, 6.1 (2s, 2H, CH$_2$=C)	60.9	9.8	63.2	10.5
Myristoyl PEO(8–9) methacrylate ($\text{MEO}_{8-9}(\text{CO})\text{C}_{13}$)	0.9 (m, 3H, CH$_3$), 1.3 (br s, 22H, CH$_2$), 1.9 (s, 3H, =CCH$_3$), 2.3 (m, 2H, CH$_2$COO), 3.7 (m, 30H, CH$_2$OCH$_2$), 4.3 (m, 4H, COOCH$_2$), 5.6, 6.1 (2s, 2H, CH$_2$=C)	62.4	9.9	66.0	11.2
Palmitoyl PEO(8–9) methacrylate ($\text{MEO}_{8-9}(\text{CO})\text{C}_{15}$)	0.9 (m, 3H, CH$_3$), 1.3 (br s, 26H, CH$_2$), 1.9 (s, 3H, =CCH$_3$), 2.3 (m, 2H, CH$_2$COO), 3.7 (m, 30H, CH$_2$OCH$_2$), 4.3 (m, 4H, COOCH$_2$), 5.6, 6.1 (2s, 2H, CH$_2$=C)	62.6	10.0	65.8	11.0
Stearoyl PEO(8–9) methacrylate ($\text{MEO}_{8-9}(\text{CO})\text{C}_{17}$)	0.9 (m, 3H, CH$_3$), 1.3 (br s, 30H, CH$_2$), 1.9 (m, 3H, =CCH$_3$), 2.3 (m, 2H, CH$_2$COO), 3.7 (m, 30H, CH$_2$OCH$_2$), 4.3 (m, 4H, COOCH$_2$), 5.6, 6.1 (2s, 2H, CH$_2$=C)	63.8	10.8	67.5	11.6

The weights used for myristoyl ($x = 12$), palmitoyl ($x = 14$) and stearoyl chloride ($x = 16$) were 6.5 g (0.026 mol), 7.5 g (0.027 mol) and 9.1 g (0.03 mol), respectively, and the yields were 9.5 g (75.8%), 10.4 g (79.8%) and 10.1 g (74.3%), respectively.

^{1}H n.m.r. 90 MHz (CDCl$_3$) and elemental microanalytical data for the products are summarized in *Table 2*. These products will be designated $\text{MEO}_{8-9}(\text{CO})\text{C}_{x+1}$.

Synthesis of alkyl PEO monoacrylates. These were prepared from alkyl ethoxylate surfactants (Marlipals) according to equation (2). The method is exemplified with the alkyl ethoxylate having $x = 11$–13 and $y = 12$ (manufacturer's data). Acryloyl chloride (2 ml, 0.025 mol) in dichloromethane (dry, 20 ml) was added dropwise at room temperature to a stirred mixture of alkyl ethoxylate $\text{C}_{12-14}\text{EO}_{12}$ (15 g, 0.02 mol) and sodium carbonate (2.62 g, 0.025 mol) in dichloromethane (dry, 150 ml). The reaction was allowed to continue overnight. The solids were then filtered off and the solvent removed on a rotary evaporator to yield the product. This was then placed in a vacuum oven (room temperature) overnight to remove solvent residues. The weight of product obtained was 13.6 g, corresponding to a yield of 84.4%.

$$\text{CH}_3(\text{CH}_2)_x(\text{OCH}_2\text{CH}_2)_y\text{OH} \quad + \quad \text{CH}_2=\text{CHCOCl}$$

$$\downarrow \quad \begin{array}{c}\text{CH}_2\text{Cl}_2 \quad \text{Na}_2\text{CO}_3 \\ 0°\text{C}\end{array} \quad (2)$$

$$\underset{\underbrace{\phantom{\text{CH}_2=\text{CHC}}}_{A} \; \underbrace{\phantom{(\text{OCH}_2\text{CH}_2)_y}}_{\text{EO}_y} \; \underbrace{\phantom{\text{O}(\text{CH}_2)_x\text{CH}_3}}_{\text{C}_{x+1}}}{\overset{\overset{\text{O}}{\overset{\|}{}}}{\text{CH}_2=\text{CHC}}(\text{OCH}_2\text{CH}_2)_y\text{O}(\text{CH}_2)_x\text{CH}_3}$$

(for x and y see Table 1)

The weights of starting materials used and the weights and yields of products for other surfactants are shown in *Table 3*. ^{1}H n.m.r. 250 MHz (CDCl$_3$) data are shown in *Table 4*, where these compounds are designated $\text{AEO}_y\text{C}_{x+1}$, y and x referring to the manufacturer's nominal figure.

Solution free radical polymerizations of (meth)acrylated surfactants. These were carried out in small round-bottomed flasks fitted with a condenser. No attempt was made to exclude air. For thermally initiated reactions the flasks were stirred while immersed in an oil bath. For photochemically initiated reactions the flasks were irradiated within a cylindrical array of ultra-violet tubes (Rayonet R5-SO, New England U.V. Co.). Preliminary experiments were performed with Blemmer PEO350 but under essentially all the conditions employed only crosslinked insoluble gels were obtained. With lauroyl PEO monomethacrylate ($\text{MEO}_{8-9}(\text{CO})\text{C}_{12}$), a viscous oligomer, soluble in chloroform and tetrahydrofuran, was obtained when the monomer (5.0 g) was dissolved in toluene (5 ml) containing AIBN (2 wt%) and heated overnight at $\sim 100°$C. A soluble product was also obtained when this monomer (0.5 g) was copolymerized with methyl methacrylate (0.5 g) under analogous conditions. Gel permeation chromatographic analysis (see later) yielded $M_n = 1400$, $M_w = 9000$ and $M_n = 660$, $M_w = 1900$ for the copolymer and homopolymer, respectively. Other attempts to produce high-molecular-weight linear homopolymers from $\text{MEO}_{8-9}(\text{CO})\text{C}_{12}$ resulted in the formation of crosslinked products.

Results of representative examples of thermally initiated polymerizations of alkyl PEO monoacrylates are shown in *Table 5*. Photochemically initiated reactions proved to be more consistent, and following preliminary experiments using rather dilute solutions of monomer (still above their critical micelle concentration in water (see later)), a set of preparative reactions were performed as follows. A known weight of monomer was dissolved in a known weight of water. Quantacure BTC (2 wt% of monomer) and *N,N*-dimethylethanolamine (2 wt% of monomer) were added prior to u.v. irradiation overnight. The following day the solid product was obtained by freeze drying, and the soluble polymer separated from the crosslinked component upon dissolution in dichloromethane and precipitation with hexane. The conversion to polymer was essentially quantitative (*Table 6*), and was confirmed by ^{1}H n.m.r. analysis of the solid product (before separation) which showed complete

Table 3 Weights and yields of alkyl PEO monoacrylates

Preparation of	Starting materials			Weight of product (g)	Yield (%)
	Surfactant g (mol)	Acryloyl chloride ml (mol)	Sodium carbonate g (mol)		
$AEO_{14}C_{12-14}$	15 (0.018)	1.80 (0.022)	2.34 (0.022)	12.8	80.0
$AEO_{20}C_{12-14}$	15 (0.014)	1.36 (0.017)	1.78 (0.017)	13.7	87.0
$AEO_{30}C_{12-14}$	15 (0.010)	1.60 (0.020)	2.09 (0.020)	11.7	75.0
$AEO_{30}C_{18}$	20 (0.013)	1.20 (0.015)	1.65 (0.016)	20.5	97.0
$AEO_{40}C_{18}$	20 (0.010)	0.96 (0.012)	1.25 (0.012)	19.3	94.5
$AEO_{18}C_{16-18}$	20 (0.019)	4.00 (0.050)	4.00 (0.040)	19.5	93.0
$AEO_{8}C_{10}$	5 (0.010)	1.00 (0.012)	1.35 (0.013)	4.3	78.0
$AEO_{8}C_{12}$	5 (0.009)	1.00 (0.012)	1.30 (0.012)	3.5	63.5

Table 4 ^{1}H n.m.r. assignments for alkyl PEO monoacrylates

Compound	^{1}H n.m.r. resonances in $CDCl_3$, δ (ppm)
$AEO_{12}C_{12-14}$	0.9 (t, 3H, CH_3), 1.2 (m, 25H, CH_2), 3.7 (m, 53H, CH_2OCH_2), 4.3 (t, 1H, CH_2OCO), 5.7–6.5 (m, 3H, CH_2=CH)
$AEO_{14}C_{12-14}$	0.8 (t, 3H, CH_3), 1.2 (m, 20H, CH_2), 3.5 (m, 49H, CH_2OCH_2), 4.2 (t, 2H, CH_2OCO), 5.6–6.4 (m, 3H, CH_2=CH)
$AEO_{20}C_{12-14}$	0.9 (t, 3H, CH_3), 1.2 (m, 18H, CH_2), 3.6 (m, 64H, CH_2OCH_2), 4.2 (t, 1H, CH_2OCO), 5.7–6.5 (m, 2H, CH_2=CH)
$AEO_{30}C_{12-14}$	0.9 (t, 3H, CH_3), 1.2 (m, 17H, CH_2), 3.6 (m, 89H, CH_2OCH_2), 4.2 (t, 1H, CH_2OCO), 5.7–6.5 (m, 5H, CH_2=CH)
$AEO_{18}C_{16-18}$	0.9 (t, 3H, CH_3), 1.3 (m, 26H, CH_2), 3.6 (m, 69H, CH_2OCH_2), 4.3 (t, 2H, CH_2OCO), 5.7–6.5 (m, 4H, CH_2=CH)
$AEO_{30}C_{18}$	0.9 (t, 3H, CH_3), 1.3 (m, 26H, CH_2), 3.6 (m, 116H, CH_2OCH_2), 4.3 (t, 2H, CH_2OCO), 5.7–6.5 (m, 6H, CH_2=CH)
$AEO_{40}C_{18}$	0.9 (t, 3H, CH_3), 1.3 (m, 24H, CH_2), 3.6 (m, 159H, CH_2OCH_2), 4.3 (t, 2H, CH_2OCO), 5.7–6.5 (m, 7H, CH_2=CH)
$AEO_{8}C_{10}$	0.8 (t, 3H, CH_3), 1.2 (m, 16H, CH_2), 3.6 (m, 33H, CH_2OCH_2), 4.3 (t, 2H, CH_2OCO), 5.6–6.4 (m, 3H, CH_2=CH)
$AEO_{8}C_{12}$	0.8 (t, 3H, CH_3), 1.2 (m, 20H, CH_2), 3.6 (m, 33H, CH_2OCH_2), 4.3 (t, 1H, CH_2OCO), 5.6–6.4 (m, 2H, CH_2=CH)

disappearance of the vinyl resonances at δ5.5–6.5 in all cases, and broadening of the remainder. These polymeric surfactants are designated $PAEO_yC_{x+1}$.

Determination of critical micelle concentration (CMC). The *CMC*s of precursor non-ionic surfactants, acryloylated derivatives and the soluble polymers derived from the latter were determined using surface tension measurements. Details of our own particular methodology are well documented[5]. This employs a Du Nuoy tensiometer and suspended platinum ring. As before, the instrument was calibrated using pure solvents of known surface tension. Surface tension data for sets of solutions of each surfactant were recorded, and the normal plots of surface tension *versus* log(concentration) were constructed. In each case the anticipated curves were obtained and the *CMC* was read off from the sharp point of inflection. Data for the critical surface tension at the *CMC* γ_{CMC} and the gradient of the line immediately below the *CMC* were also recorded.

Table 5 Thermally initiated polymerizations of alkyl PEO mono-acrylates[a]

Monomer (g) Solvent (ml)	Initiator (wt%)	Type of polymer	Comment
$AEO_{30}C_{12-14}$ (1) Toluene (5)	AIBN (2)	Viscous liquid	c
$AEO_{30}C_{12-14}$ (4) Propanol (10)	AIBN (2)	Viscous liquid solidified overnight to low-melting-point solid	c
$AEO_{20}C_{12-14}$ (4) Propanol (10)	AIBN (2)	Very viscous liquid	c
$AEO_{14}C_{12-14}$ (4) Propanol (10)	AIBN (2)	Very viscous liquid	c
$AEO_{12}C_{12-14}$ (4) Propanol (10)	AIBN (2)	Viscous liquid	c
$AEO_{30}C_{12-14}$ (0.2023) Water (250) (above the *CMC*)	$S_2O_4^{2-}$ (2)	Very viscous liquid	d
$AEO_{30}C_{12-14}$ (0.0244) Water (250) (below the *CMC*)	$S_2O_4^{2-}$ (2)	Very viscous liquid	d
$AEO_{30}C_{12-14}$ (3) (bulk)	AIBN (2)[b]	Crosslinked polymer	e
$AEO_{12}C_{12-14}$ (3) (bulk)	AIBN (2)[b]	Crosslinked polymer	e

[a] 12 h at 70°C
[b] At 80°C
[c] Product was precipitated with hexane and was soluble in a range of organic solvents
[d] Product was isolated by freeze drying and was soluble in a range of organic solvents
[e] Insoluble in all solvents tested

Application of the Gibbs absorption isotherm allowed the surface area occupied by each surfactant molecule (*A*) to be calculated from the experimental gradients. The results obtained are gathered together in *Table 7*.

Cloud points of surfactants. Non-ionic surfactants in water become desolvated on heating and eventually phase separated at the cloud points. Data for the range of alkyl ethoxylates studied were determined using a 2 wt% solution of surfactant in a 10 wt% NaCl solution. The results are shown in *Table 8*.

The acrylated species and their corresponding polymers displayed cloudy solutions in water (2 wt%) even at room temperature and remained cloudy at 0°C. To derive some measure of relative water solubility,

Table 6 Photochemically initiated polymerizations of alkyl PEO monoacrylates

Monomer (g)	Water (ml)	Polymer Soluble (%)	Polymer Insoluble (%)	Soluble polymer M_n	Soluble polymer M_w	Soluble polymer Polydispersity
$AEO_{12}C_{12-14}$ (5)	75	66	34	8100	13 100	1.6
$AEO_{14}C_{12-14}$ (5)	100	16	84	4200	10 500	2.5
$AEO_{20}C_{12-14}$ (5)	25	92	8	4800	11 700	2.5
$AEO_{30}C_{12-14}$ (5)	50	58	42	6900	14 100	2.1
$AEO_{18}C_{16-18}$ (5)	25	0	100	–	–	–
$AEO_{30}C_{18}$ (5)	100	10	90	4800	14 100	3.0
$AEO_{40}C_{18}$ (5)	100	66	34	1400	12 700	9.3
$\{AEO_{30}C_{12-14}(5)\}$ $\{HEMA^a(5)\}$	25	17	83	2600	7400	2.9
$\{AEO_{20}C_{12-14}(5)\}$ $\{HEMA(5)\}$	25	28	72	–	–	–
$\{AEO_{12}C_{12-14}(5)\}$ $\{HEMA(5)\}$	25	24	76	5200	8300	1.6
AEO_8C_{10} (1)	20	100	0	–	–	–

^{a} HEMA = hydroxyethyl methacrylate

Table 7 Critical micelle concentration data for surfactants

Surfactant	10^{-5} CMC (mol dm^{-3})	γ_{CMC} (mN m^{-1})	Area occupied by a surfactant molecule, 10^{19} A (m^2)	Free energy of micellization ΔG, (kJ mol^{-1})
Surfactant $HO(EO)_{12}C_{12-14}$	8.9	33	6.5	−23
$HO(EO)_{14}C_{12-14}$	10.0	36	7.5	−23
$HO(EO)_{20}C_{12-14}$	11.2	39	10.0	−23
$HO(EO)_{30}C_{12-14}$	31.60	44	15.0	−20
Acrylated surfactant $AEO_{12}C_{12-14}$	4.5	33	6.0	−25
$AEO_{14}C_{12-14}$	5.3	34	6.5	−24
$AEO_{20}C_{12-14}$	6.7	37	8.0	−24
$AEO_{30}C_{12-14}$	13.3	43	11.0	−22
Polymer surfactant $PAEO_{12}C_{12-14}$	9.1	35	5.5	−23
$PAEO_{14}C_{12-14}$	12.3	34	6.5	−22
$PAEO_{20}C_{12-14}$	17.8	40	9.0	−21
$PAEO_{30}C_{12-14}$	28.8	45	12.0	−20
Surfactant $HO(EO)_{30}C_{18}$	2.8	43	6.5	−26
$HO(EO)_{40}C_{18}$	3.2	50	12.0	−26
Acrylated surfactant $AEO_{30}C_{18}$	1.3	43	5.0	−28
$AEO_{40}C_{18}$	1.4	49	8.5	−28
Polymer surfactant $PAEO_{30}C_{18}$	5.6	40	6.5	−24
$PAEO_{40}C_{18}$	7.5	47	12.5	−24
$PAEO_{12}C_{12-14}$/HEMA (50/50)	4.7	35	5.5	−25
$PEO_{12}C_{12-14}$/HEMA (50/50)	26.6	44	11.0	−20

Table 8 Cloud points of alkyl ethoxylates and water weight turbidity values ($WWTV$) of their derivatives

2% surfactant in 10% NaCl aqueous solution	Cloud point (°C)	2% surfactant in 2-ethoxyethanol	$WWTV$ (g)	2% surfactant in 2-ethoxyethanol	$WWTV$ (g)
$EO_{12}C_{12-14}$	67–68	$AEO_{12}C_{12-14}$	2.1	$PAEO_{14}C_{12-14}$	0.7
$EO_{14}C_{12-14}$	74–75	$AEO_{14}C_{12-14}$	3.1	$PAEO_{20}C_{12-14}$	2.2
$EO_{20}C_{12-14}$	77–78	$AEO_{20}C_{12-14}$	4.2	$PAEO_{30}C_{12-14}$	No turbidity observed, i.e. infinite
$EO_{30}C_{12-14}$	79–80	$AEO_{30}C_{12-14}$	5.4	$PAEO_{30}C_{18}$	3.8
$EO_{30}C_{18}$	79–82	$AEO_{30}C_{18}$	2.3	$PAEO_{40}C_{18}$	14.4
$EO_{40}C_{18}$	77.5–83.5	$AEO_{40}C_{18}$	0.5	$PAEO_{30}C_{12-14}$/HEMA (50/50)	4.8
		$PAEO_{12}C_{12-14}$	Cloudy on dissolution	$PAEO_{12}C_{12-14}$/HEMA (50/50)	4.3

therefore, each sample was dissolved in 2-ethoxyethanol (2 wt%) and water was added dropwise at room temperature. The volume of water required to cause turbidity was noted and termed the 'water weight turbidity value' ($WWTV$). The data are shown in *Table 8*.

Use of polymerizable surfactants as sole emulsifiers in emulsion polymerizations. Small batch emulsion polymerizations were carried out using a photochemical initiator system with (separately) styrene, methyl methacrylate and vinyl acetate.

Typically, surfactant (0.1 g), Quantacure BTC (0.01 g), N,N-dimethylethanolamine (0.01 g) and monomer (1 ml) were added to water (10 ml) in a small glass flask fitted with a condenser. In each case an emulsion formed readily on shaking, and then this was stirred and irradiated overnight (12 h) within an array of u.v. tubes to yield a white emulsion polymer latex. For comparison, the structurally analogous, conventional non-ionic surfactants were also used in the same way. The results are summarized in *Table 9*.

Latex flocculation studies. The resistance of polymer latices to flocculation with added electrolyte and thermal shock was examined as follows using polystyrene emulsions. Small samples (1 ml) of each polymer latex were thoroughly shaken. Various electrolyte solutions (1 ml) were then added, one to each sample. The electrolytes were chosen to contain mono-, di- and trivalent anions, and mono-, di- and trivalent cations at concentrations of 1 and 5 M (or saturated if the water solubility was low). The salts used were sodium chloride, soldium sulfate, trisodium orthophosphate, calcium chloride and aluminium chloride (hexahydrate). Each latex sample was also subjected to a freeze–thaw cycle. The results are summarized in *Table 10*.

Equipment

^{1}H n.m.r. spectra were recorded on a Perkin–Elmer R32 90 MHz spectrometer or a Bruker WM 250 MHz spectrometer. Elemental microanalyses were performed on a Carlo Erba Analyser 1106. Equilibrium surface tensions were measured using a tensiometer supplied by Cambridge Instrument Co. Ltd. Gel permeation chromatography (g.p.c.) was carried out with tetrahydrofuran as the eluent and columns from Polymer Laboratories.

Table 9 Emulsion polymerizations using alkyl ethoxylate surfactants and their acrylated analogues

Monomer	Surfactant	Emulsion latex appearance 15 min after polymerization
Methyl methacrylate	$EO_{30}C_{12-14}$	Small amount of precipitated solid, essentially still an emulsion
Methyl methacrylate	$AEO_{30}C_{12-14}$	Almost 100% creaming, clear solution
Vinyl acetate	$EO_{30}C_{12-14}$	Substantial creaming but essentially still an emulsion
Vinyl acetate	$AEO_{30}C_{12-14}$	100% creaming, clear solution
Styrene	$EO_{30}C_{12-14}$	Stable emulsion
Styrene	$AEO_{30}C_{12-14}$	Stable emulsion
Methyl methacrylate	$EO_{12}C_{12-14}$	Almost 100% creaming, clear solution
Methyl methacrylate	$AEO_{12}C_{12-14}$	Substantial creaming
Vinyl acetate	$EO_{12}C_{12-14}$	Some creaming but essentially still an emulsion
Vinyl acetate	$AEO_{12}C_{12-14}$	100% creaming, clear solution
Styrene	$EO_{12}C_{12-14}$	Small amount of creaming but essentially still an emulsion
Styrene	$AEO_{12}C_{12-14}$	100% creaming, clear solution

Polystyrene standards were used for calibration and the data adjusted using the universal calibration method employing the Mark–Houwink parameters for poly(methyl methacrylate). It was felt that this adjustment might provide data somewhat closer to reality than raw polystyrene equivalents.

DISCUSSION

Synthesis of alkanoyl PEO monomethacrylates

The availability of a range of PEO monomethacrylates from the Nippon Oil and Fats Co. seemed to us to provide a facile one-step route to polymerizable non-ionic surfactants (equation (1)), and in addition it was felt that the ester linkage between the hydrophobe and the hydrophile might aid the (bio)degradability of these surfactants. The preparations were eventually carried out cleanly and in reasonable yields as indicated. Initially it was expected that ethoxylate lengths of eight units would yield completely water-soluble surfactants via hydration of the ether oxygens. On acylation the hydroxy group of the PEO monomethacrylate is converted to the less-polar

Table 10 Flocculation studies on polystyrene lactices produced using alkyl ethoxylate $EO_{30}C_{12-14}$ and its acrylated analogue

	Conventional surfactant		Acrylated surfactant	
Additive	Time zero	After one week	Time zero	After one week
1 M NaCl 5 M NaCl 1 M Na$_2$SO$_4$ Na$_2$SO$_4$ (sat.) Na$_3$PO$_4$ (sat.) 1 M CaCl$_2$ 5 M CaCl$_2$ 1 M AlCl$_3$·6H$_2$O AlCl$_3$·6H$_2$O (sat.)	White emulsion retained	Still white emulsion containing small amount of precipitated solid	White emulsion retained	Completely phase separated to give a clear solution and a precipitated solid
Freeze–thaw, then warm to room temperature	White emulsion retained	White emulsion containing small amount of solid	Clear solution containing precipitated solid	Clear solution containing precipitated solid

ester function. As a result the hydrophilicity of the original Blemmer PEO350 drops significantly and the lauroyl, myristoyl, palmitoyl and stearoyl derivatives all proved to be rather water insoluble. A surface tension plot *versus* log(concentration) for the myristoyl derivative is shown in *Figure 1*, and this clearly lacks the sharp features characteristic of a soluble surfactant. At concentrations above $\sim 10^{-4}$ M the solutions are extremely cloudy and are complex colloidal suspensions, and completely clear solutions are obtained only at very low concentrations. No clear transition is detectable. Shorter-chain acid chlorides (C$_5$ and C$_7$) were employed (details not recorded here) in an attempt to improve the water solubility of the alkanoyl PEO350 monomethacrylates, and this was successful. However, the alkyl chain lengths proved too short for these materials to be surface active, and no *CMC* feature was detectable.

The rather low hydrophilic–lipophilic balance (*HLB*) values of these alkanoyl derivatives surprised us a little and prohibited further exploitation in aqueous solutions, but it is clear that these species could offer opportunities for use as polymerizable water-in-oil emulsifiers.

Synthesis of alkyl ethoxylate monoacrylates

The work above demonstrated that ethoxylate lengths in excess of eight would be required to produce water-soluble, non-ionic surfactants when no terminal OH group is present. Suitable commercially available alkyl ethoxylates were identified with a view to acrylating the terminal OH group (equation (2)). This apparently straightforward modification was not without its problems. Prior to using sodium carbonate as the base to absorb the HCl formed, organic bases such as pyridine and triethylamine were tried. However, in some cases the heat generated on the addition of the acryloyl chloride caused charring of the product despite the flask being ice cooled. Filtration of the triethylamine (or pyridinium) hydrochloride salt formed was very slow even under vacuum and the fine crystals tended to block the pores of the sinter filter funnel. The major problem, however, was that removal of any excess organic base by washing with dilute acid led to severe emulsification. Use of solid sodium carbonate, however, allows a complete non-aqueous work up, and this transformed the syntheses. The products are tacky, wax-like solids and are difficult to purify. Being acrylates they are also liable to polymerize, and so the materials were exploited as isolated and described in the Experimental section.
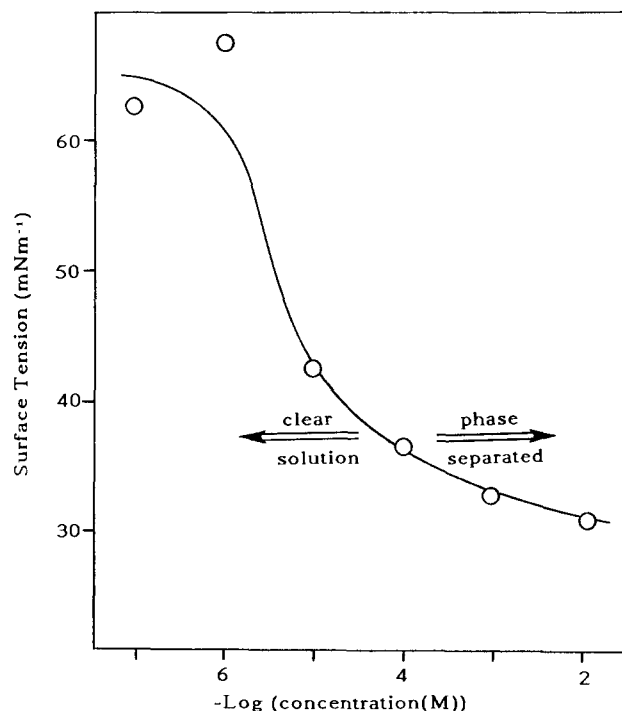
Figure 1 Air/water surface tension *versus* log(concentration) for myristoyl PEO(8–9) monomethacrylate

[1]H n.m.r. analysis of the starting alkyl ethoxylates (*Table 1*) indicated that the 'real' structures of the molecules generally differed from the nominal structures stated by the manufacturer. The largest deviation occurs with the species with high EO contents. In one instance the actual EO content is much lower than specified (Marlipal 1850/30) and in another much larger (Marlipal 1850/40). These variations are normal and arise from the method of manufacture. Not surprisingly, the monodisperse research sample from Nikko conformed well with its specified structure.

Yields of the acrylated derivatives (*Table 3*) were always good once the sodium carbonate proceudre was employed. Confirmation of acylation was only possible using 250 MHz [1]H n.m.r. spectroscopy. 90 MHz spectra failed to display the acrylate protons present in only low abundance. A careful analysis of the splitting pattern of the vinyl ester – two sets of doublets at $\sim \delta 5.8$, four singlets at $\sim \delta 6.0$ and another two sets of doublets at $\sim \delta 6.4$ – confirmed successful acrylation.

Polymerization of (meth)acrylated surfactants

Bulk polymerizations of Blemmer PEO350 and its alkanoylated derivatives using AIBN and benzoyl peroxide at 70°C resulted in highly intractable crosslinked material, completely insoluble in all solvents tested. This presumably arises from a significant level of dimethacrylated contaminant in the Blemmer PEO350 carried over into the alkanoylated derivatives. A soluble 'homopolymer' of the lauroyl species and a soluble 'copolymer' of this with methyl methacrylate were obtained by solution polymerization in toluene with AIBN as initiator. However, the M_n values of these, 660 and 1400 respectively, show them to be telomers of only two or three monomer units.

Bulk and solution thermally initiated polymerizations of the alkyl PEO monoacrylates yielded only low-molecular-weight telomers, again typically di- and trimeric, or insoluble crosslinked species. However, photochemically initiated reactions in water did yield significant levels of soluble products with reasonable M_n values (*Table 6*). The initator system employed was of the ketone/amine type, and though only the results with Quantacure BTC are quoted here other similar initiators proved equally effective. The systems have been extensively researched recently[15,16]. Polymerizations were essentially quantitative with the ratio of linear to crosslinked polymer varying widely and non-systematically. The nominal molecular weights of the soluble fraction suggest four to 10 monomer units for the species $PAEO_yC_{12-14}$, and unlike the telomers above, these products are solids rather than viscous liquids. There are insufficient data to be definitive but it seems that homopropagation becomes easier as the EO chain length in the monomer becomes shorter. This would be consistent with the known behaviour of macromer species. The tendency for the degree of polymerization to be consistently higher with the photochemically initiated reactions in water is not clear, but it may be due to the aggregated form of these monomers (above their *CMC*).

The inevitable formation of some crosslinked product was a major disappointment and is not readily explained. In principle, the monomer syntheses should not generate any diacrylate (crosslinker) as a contaminant. Earlier reports exist of mono(meth)acrylates of monomethyl poly(ethylene glycol)s gelling on polymerization[17], not as a result of covalent crosslinking, but from the occurrence of strong stereocomplexes formed via stereoregular sequences in the polymer[18,19]. In addition, when Ito et al.[9] used a similar monomer to the ones investigated here in aqueous dispersion copolymerizations of styrene and benzyl methacrylate, insoluble gels were formed at high conversion.

Our own view, however, still favours the idea of diacrylate contaminant and indeed this could arise if the original surfactants were themselves contaminated with free oligo(ethylene glycol)s. Discussions with manufacturers suggest that this is a real possibility. The purity of the Nikko research grade sample, however, was much better and in particular it was believed to contain no glycol. Although the acrylated monomer derived from this material proved to have only low solubility in water, it was polymerized under similar conditions to the Marlipal derivatives and indeed it did yield ~100% soluble polymer product. This therefore tends to confirm that the insoluble fractions obtained

earlier are indeed due to the presence of diacrylate contaminants.

MICELLIZATION

Surfactants and acrylated surfactants

The data for the precursor non-ionic surfactants in *Table 7* are in excellent agreement with recently published data on structurally similar species[20]. Indeed, the level of agreement is most rewarding for the two research groups involved. The present data (*Table 7*) show that, for all series of surfactants, as the length of the ethoxylate chain increases the *CMC* correspondingly increases. This is more apparent in *Figure 2*, and is, of course, totally consistent with the hydrophilicity rising with the degree of ethoxylation. The dependence is extremely weak with the series EO_yC_{18} and AEO_yC_{18} which have very high nominal ethoxylate lengths (> 30), and suggests that the *CMC* begins to level to some maximum value in any non-ionic series of this type. This seems reasonable since a point must be reached when hydrophilicity is essentially maximized (for a given hydrophobe). At this point the main determinant is likely to be the length of the hydrophobe, and this is seen clearly in *Figure 2* for species with a nominal ethoxylate length of 30. The *CMC*s of those surfactants with a C_{18} hydrophobe are much lower than those with the C_{12-14} hydrocarbon chain.

Comparison of the data for EO_yC_{12-14} with those of AEO_yC_{12-14} (i.e. the starting alkyl ethoxylates and their acrylated derivatives) shows a consistent reduction in the *CMC*. This is presumably due to the fall in hydrophilicity on loss of the terminal OH group. The same change is seen in the EO_yC_{18} and AEO_yC_{18} series. The magnitude of the fall in the *CMC* surprised us, and seems larger than expected from simply methylating the terminal OH group of an alkyl ethoxylate. In general, acrylation reduces *CMC*s by about a factor of two.

Polymers

The very presence of a discrete *CMC* transition for the 'polymeric' surfactants ($PAEO_yC_{12-14}$, $PAEO_yC_{18}$, $PAEO_yC_{12-14}/$HEMA) indicates that micelles are formed by interaction of a number of polymer chains. Initially it was thought that micelles may have been formed from *individual* polymer chains. Had this been the case it can be argued that the surface tension would have remained at a fixed value independent of concentration. This might be the value for water (approximately $70\,mN\,m^{-1}$) if no polysurfactant became absorbed at the air–water interface, or it might have been a typical value for the surface tension at the *CMC* of a non-ionic surfactant if the polysurfactant was absorbed strongly at the interface. In any event this situation did not arise and normal surface tension/concentration behaviour was observed. This is perhaps not surprising since these 'polymers' are only oligomeric (at best 10 monomer units). Stable micelles normally require at least 50 surfactant units, and in this case there are insufficient numbers for one polymer chain to achieve intramolecular micellization.

On polymerization to give the $PAEO_yC_{12-14}$ and $PAEO_yC_{18}$ species, the presence of the hydrophobic, saturated hydrocarbon polymer backbone might be expected to reduce the *CMC* as it increases the overall hydrophobicity. However, this is clearly not the case (*Figure 2*, compare $PAEO_yC_{18}$ to AEO_yC_{18}). The
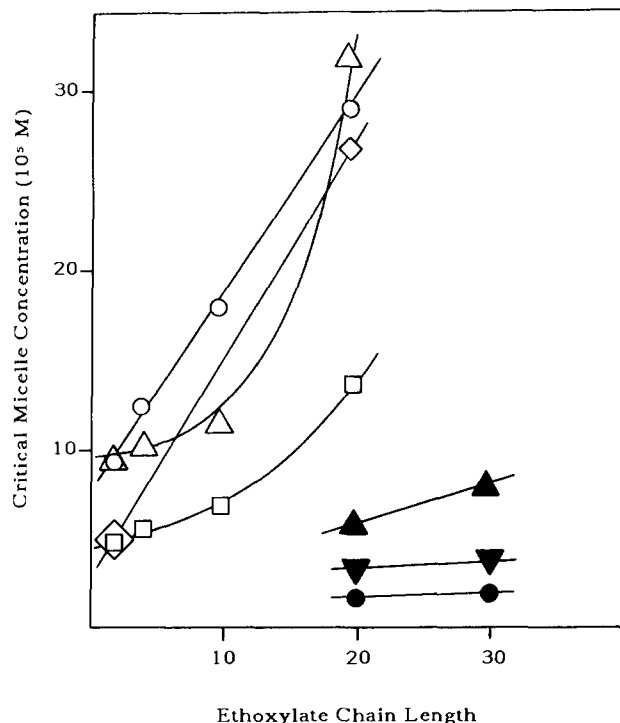
Figure 2 Critical micelle concentration CMC as a function of ethoxylate chain length: ($\triangle$) EO_yC_{12-14}; ($\square$) AEO_yC_{12-14}; ($\bigcirc$) $PAEO_yC_{12-14}$; ($\diamondsuit$) $PAEO_yC_{12-14}$/HEMA (50/50 copolymer); ($\blacktriangledown$) EO_yC_{18}; ($\bullet$) AEO_yC_{18}; ($\blacktriangle$) $PAEO_yC_{18}$

CMCs of the polymers are higher, and in most cases approximately double those of their monomeric counterparts. Why this is so is not clear, but one possibility is that the polymer backbone inhibits facile formation of the conformation required to allow packing in a micelle. Such steric restriction could well manifest itself as a rise in the CMC.

The 50/50 surfactant/HEMA copolymers ($PAEO_{12}$ C_{12-14}/HEMA and $PAEO_{30}C_{12-14}$/HEMA) were anticipated to have higher CMCs than the homopolymers ($PAEO_{12}C_{12-14}$ and $PAEO_{30}C_{12-14}$) because of the presence of the hydrophilic HEMA segments. However, if the argument about steric restriction in the packing of the polysurfactant is correct, such restriction might be lifted in the case of the HEMA copolymer. The CMC might therefore be expected to fall when HEMA segments are present. This in fact proved to be the case and adds substance to the steric restriction argument.

Critical surface tension γ_{CMC}

For the series EO_yC_{12-14}, AEO_yC_{12-14}, $PAEO_yC_{12-14}$ the ability of a given surfactant structure to reduce the surface tension appears to be unrelated to whether it is present in the free, acrylated or polymeric form. The main factor governing surface tension reduction appears to be the ethoxylate chain length (*Figure 3*). As the ethoxylate length increases, the critical surface tension also increases, i.e. the ability of the surfactant to reduce the surface tension is inversely proportional to its ethoxylate length. The same trend is also evident in the EO_yC_{18}, AEO_yC_{18}, $PAEO_yC_{18}$ series. The value of γ_{CMC} is probably controlled by the density of packing of hydrocarbon chains at the air–water interface. The more dense the packing, the closer γ_{CMC} approaches the surface tension for an aliphatic hydrocarbon. Clearly, the shorter ethoxylate chains allow tighter packing to minimize γ_{CMC}.

If this picture is correct it should be reflected in the area data. Indeed, this is so; in *Figure 4* the area occupied per molecule is seen to fall progressively as the ethoxylate length is reduced.

In contrast to the degree of ethoxylation, the length of the hydrophobe seems to have little effect on the ability of the surfactant to reduce the surface tension (e.g. for $EO_{30}C_{12-14}$ $\gamma_{CMC} = 44.0$ mN m^{-1} and for $EO_{30}C_{18}$ $\gamma_{CMC} = 43.4$ mN m^{-1}), at least in the range studied here.

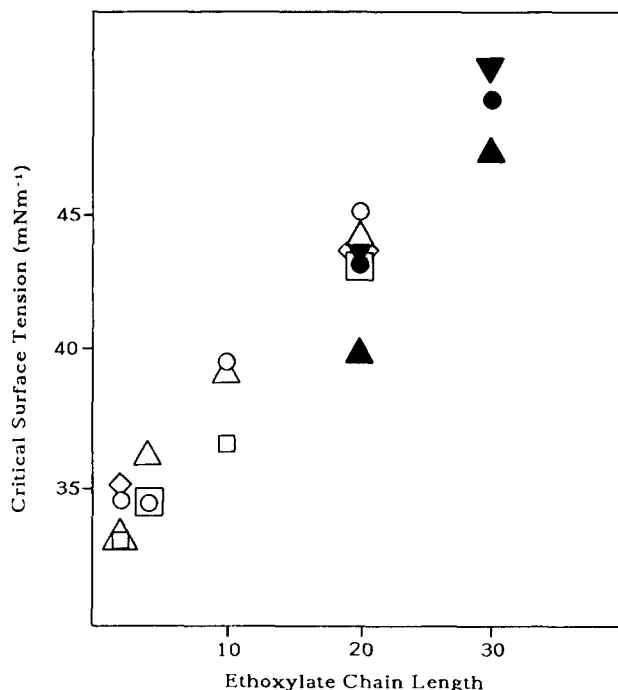**Figure 3** Critical surface tension γ_{CMC} as a function of ethoxylate chain length: ($\triangle$) EO_yC_{12-14}; ($\square$) AEO_yC_{12-14}; ($\bigcirc$) $PAEO_yC_{12-14}$; ($\diamondsuit$) $PAEO_yC_{12-14}$/HEMA (50/50 copolymer); ($\blacktriangledown$) EO_yC_{18}; ($\bullet$) AEO_yC_{18}; ($\blacktriangle$) $PAEO_yC_{18}$
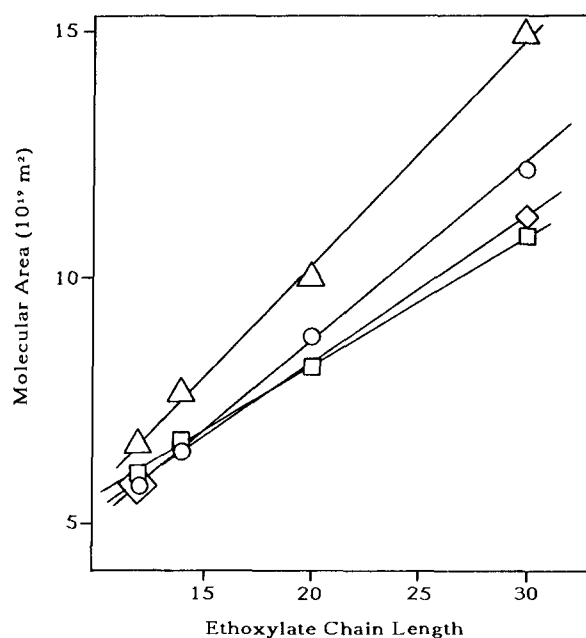

Figure 4 Area occupied at the air/water interface by a surfactant molecule as a function of ethoxylate chain length: ($\triangle$) EO_yC_{12-14}; ($\square$) AEO_yC_{12-14}; ($\bigcirc$) $PAEO_yC_{12-14}$; ($\diamondsuit$) $PAEO_yC_{12-14}$/HEMA (50/50 copolymer)

This suggests that the hydrophobes pack similarly irrespective of length and are probably in an extended-chain conformation where length would not be expected to play a major role. However, the picture is not entirely tidy because for a given ethoxylate length the molecular area occupied when the hydrophobe is C_{18} is lower than when it is C_{12-14} (for surfactant, acrylated surfactant and polysurfactant) – perhaps reflecting the stronger integrated van der Waals forces for the longer chain.

Cloud points and the water weight turbidity value (WWTV)

The cloud points for the original alkyl ethoxylates are plotted as a function of ethoxylate chain length in *Figure 5*. The data agree well with the manufacturer's information sheet, and the tendency to a limiting upper value at high ethoxylate content is consistent with a limiting hydrophilicity being achieved. The higher value for $EO_{30}C_{18}$ over $EO_{30}C_{12-14}$ is surprising but these are nominal structures, and our own ^1H n.m.r. data (*Table 1*) suggest effective structures perhaps more in keeping with these results.

Our own water compatibility parameter ($WWTV$) data are plotted in *Figure 6*. In general the trend is as expected, that higher degrees of ethoxylation give better water tolerance and turbidity is induced only with increasing levels of added water. There is, however, one exception, the acrylated species AEO_yC_{18}, where the $WWTV$ falls when y is increased from 30 to 40. This is difficult to accommodate, especially when the polymers derived from these, $PAEO_yC_{18}$, show the steepest dependence in the anticipated direction. Another apparent anomaly is with the two HEMA copolymers $PAEO_{30}C_{12-14}$/HEMA and $PAEO_{12}C_{12-14}$/HEMA. The latter shows an increase in $WWTV$ relative to the $PAEO_{12}C_{12-14}$ homopolymer, in keeping perhaps with the increase in hydrophilicity expected when HEMA is incorporated. However, the former shows a fall in $WWTV$ relative to its homopolymer, and this is difficult to explain. It must be emphasized that the data sample here is very low and considerably more work is required with these systems before any firm conclusions are drawn.
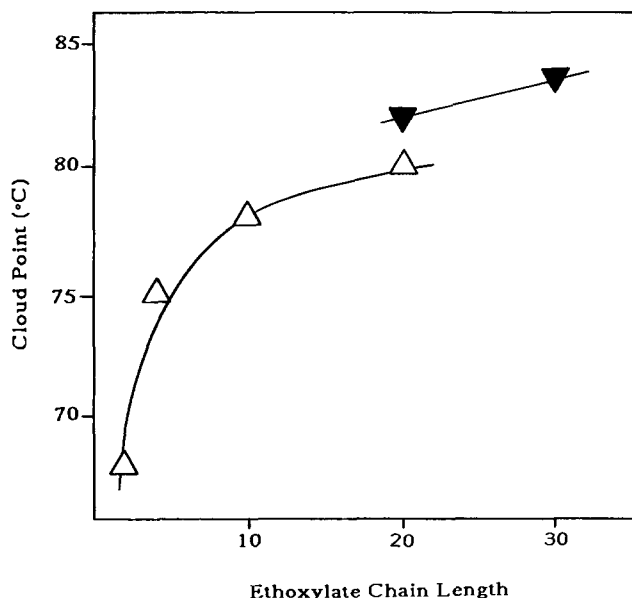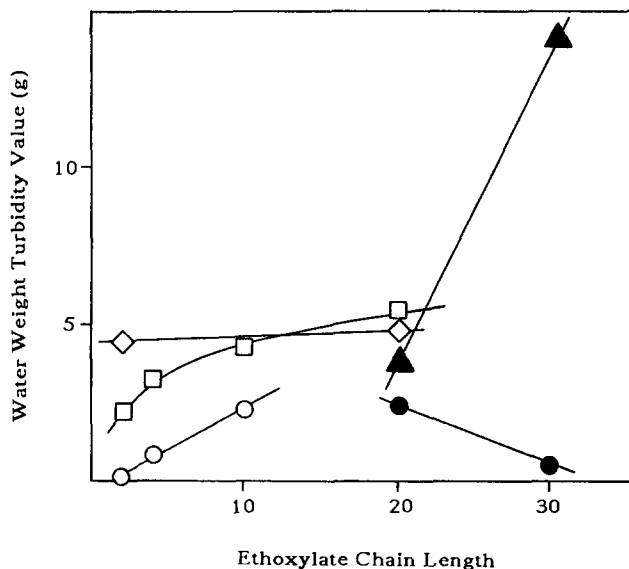

Figure 6 Water weight turbidity value of surfactant as a function of ethoxylate chain length: (□) AEO_yC_{12-14}; (○) $PAEO_yC_{12-14}$; (◇) $PAEO_yC_{12-14}$/HEMA (50/50 copolymer); (●) AEO_yC_{18}; (▲) $PAEO_yC_{18}$

Emulsion polymerization and flocculation studies

One possible use of a polymerizable surfactant is as a replacement for or adjunct to normal low-molecular-weight surfactants in emulsion polymerization systems. Polymerizable surfactants might be expected to become incorporated into the surface of emulsion particles and might impart increased stability to the resultant latex. Chemically bound surfactant would not be free to migrate and may provide, for example, better resistance to moisture in film-formed latices. This idea is by no means a new one and an early report described the use of this approach to make emulsion particles of defined size and bound surface charge[21].

In the present work it has been possible to compare the behaviour of a range of conventional alkyl ethoxylate surfactants in emulsion polymerizations with their acrylated analogues. This has allowed us to make a direct comparison of identical surfactant structures, one of which remains kinetically mobile in the resultant latices, while the other becomes chemically bound to the latex particles. The surfactants chosen for this detailed study were $EO_{30}C_{12-14}$ with $AEO_{30}C_{12-14}$ and $EO_{12}C_{12-14}$ with $AEO_{12}C_{12-14}$ as examples at the extremes of the *HLB* range available. In all cases both groups of surfactants emulsified the monomers styrene, methyl methacrylate and vinyl acetate, and superficially during polymerization there was no difference between the conventional surfactants and their polymerizable analogues. When polymerization was complete (12 h), stirring was stopped and each latex examined visually 15 min later (*Table 10*). In the case of the methyl methacrylate and vinyl acetate systems the polymerizable surfactants yield much *less* stable emulsions than their non-polymerizable analogues. Essentially complete creaming of latex particles occurs with the bound surfactant, while stable emulsions were found with the kinetically mobile analogues. The only exception was the poly(methyl methacrylate) latex with the low *HLB* surfactant $EO_{12}C_{12-14}$, which also displayed substantial creaming. The situation with styrene polymerizations, however, was quite different. The low *HLB* surfactants $EO_{12}C_{12-14}$ and $AEO_{12}C_{12-14}$

Figure 5 Cloud point as a function of surfactant ethoxylate chain length: (△) EO_yC_{12-14}; (▼) EO_yC_{18}

behaved as with methyl methacrylate and vinyl acetate; however, the high *HLB* species $EO_{30}C_{12-14}$ and $AEO_{30}C_{12-14}$ *both* yielded very stable emulsions, so much so that these were available for flocculation studies.

Addition of different electrolyte types to the two stable polystyrene latices (*Table 10*) essentially yielded the same result. Initially, both sets of emulsions were stable, but those prepared with the polymerizable surfactant showed progressive signs of destabilization. One week after the exposure to electrolyte all of the latter had precipitated to leave clear supernatants. The appearance of latices prepared with the conventional surfactants varied a little with the electrolyte added, but in general after one week a major proportion of each emulsion remained stable with only minor amounts precipitated. Similar results were obtained with the freeze–thaw cycle. The conventionally stabilized polystyrene latex remained stable one week later, while the species with the bound surfactant was found to be precipitated on thawing.

Both conventional and polymerizable alkyl ethoxylates are more effective in stabilizing polystyrene particles than both poly(methyl methacrylate) and poly(vinyl acetate) particles. This appears to be related to the greater hydrophobicity of polystyrene, which may simply offer more effective interaction with the hydrophobe of the surfactant. In turn this may well allow tighter packing at the particle surface and hence increased particle stability. The alkyl ethoxylates with the longer ethoxylate chains (i.e. the higher *HLB* species) are also the more effective. Probably two factors are involved here. The first is simply the level of water solubility, and this is common to all surfactants, irrespective of the nature of the head group. The overall level of water solubility imparted to the whole surfactant by the head group must be sufficiently high for stabilization effects to be realized. Clearly, alkyl ethoxylates with longer ethoxylate chains are more water soluble. The second factor concerns the *specific* mechanism by which alkyl ethoxylates impart stabilization. There is almost certainly at least a component of steric stabilization involved. The various theories here [22–26] all predict improved stabilization with larger repelling random coils, and hence longer ethoxylate chains would be expected to be better than shorter ones. The results here agree with those reported recently by ICI scientists[27]. They employed essentially non-surface-active methoxy-capped PEO acrylates and methacrylates as stabilizers in acrylate and styrene emulsion polymerization systems. The resulting latices showed excellent electrolyte tolerance and freeze–thaw stability, but ethoxylate chain lengths with molecular weights of 1500, and preferably 2000, were required to generate substantial positive effects. This corresponds to 35–45 EO units, even longer than the species $EO_{30}C_{12-14}$ used in this work.

Regarding the issue of conventional *versus* polymerizable surfactant, it is clear from our work here that the polymerizable species are significantly *less* effective as latex stabilizers than their simple analogues. This was somewhat disappointing, but we believe it will not be a generality when optimized structures are designed and evolved. With the present species the polymerizable acrylate group is located at the hydrophilic end of the amphiphile and so incorporation of this into macromolecules in the surface of particles would require the hydrophilic EO chain to loop back on itself to allow the hydrophobic alkyl chain also to adsorb to the particle surface. Even if this is achievable the level of stabilization generated from such short hydrophilic loops is likely to be low. This potential shortcoming was appreciated at the outset of the work, but such structures are readily accessed in synthetic terms. A more satisfactory structural design would involve the polymerizable group at the hydrophobic end with the hydrophilic EO chain possessing a free OH group. The synthesis of such molecules is, however, more problematical, and structurally well-defined species would require protection group strategies to reach them.

A second possible factor explaining the poorer performance of the polymerizable surfactant is the question of the locus of its polymerization. If such molecules have sufficient hydrophobicity it might be that significant wastage occurs by copolymerization within the cores of latex particles. For an effective contribution to stabilization the location of the polymerized unit must of course be in the surface of the particles. The use of non-surface-active polymerizable PEO mono(meth)acrylates as emulsion stabilizers clearly maximizes the chances of the hydrophilic chains being located at the surface of the particles[27], but also offers the prospect of wastage to polymerization in the aqueous phase. Clearly there is an opportunity to design optimum structures here, and we are currently pursuing this idea. Recently it has been reported that polymerizable surfactants with a low tendency to homopolymerize but with a high tendency for 1/1 copolymerization with appropriate monomers become heavily concentrated in the surface of latex particles and provide remarkable stabilization[28]. Once again, this result indicates the design possibilities which exist.

A final factor worthy of consideration is a thermodynamic one. Surface-active species in water above their *CMC*s are often regarded as pseudo phase separated or forming a discrete pseudo-phase. Thermodynamic stability is achieved only by the hydrophobic chains removing themselves from the aqueous environment – largely an entropic effect. Some time ago we were surprised when micellized polymerizable cationic surfactants precipitated when polymerized[5]. In retrospect we have rationalized this on entropic grounds. Micellized systems are close to undergoing complete phase separation and any unfavourable shift in the standard free energy of the system could cause precipitation. The process of polymerizing surface-active molecules removes a considerable degree of freedom from the system, i.e. reduces the entropy. This factor alone may be sufficient to destabilize micellar systems. If this argument is correct, similar factors are likely to operate when surfactants are employed in emulsion polymerization. A significant contribution to emulsion particle stability could well be the very dynamics of surfactant migration and exchange – essentially an entropic contribution. Covalent attachment of surfactant to particle surfaces freezes out this entropic contribution and, if the free energy is not to rise, other compensating (enthalpic) contributions must be sought. Again, these ideas can be fed into surfactant design and we are also pursuing this idea at the moment.

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