

Novel quaternary ammonium amphiphilic (meth)acrylates: 2. Thermally and photochemically initiated polymerizations

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A number of novel polymerizable quaternary ammonium (meth)acrylates have been polymerized in water at concentrations both above and below their critical micelle values, and also in isotropic alcohol solutions. Oligomeric species with \overline{DP}_n up to 25 are formed readily from micellized solutions using both photochemical and thermal initiation systems. Below critical micelle concentrations, however, polymerization seems very inefficient and conversions are very low. Even in isotropic alcohol solutions, polymerization remains sluggish and \overline{DP}_n values are typically very low, $\sim 2-4$. In dilute aqueous solution and in alcohols, it appears that charge repulsion is an obstacle to propagation, both for monomers where the cationic charge is located near the polymerizable group and for those where the charge is more remote. Radical transfer is probably more favoured. On micellization, this charge repulsion is overcome by the favourable thermodynamics of micelle formation and monomers are closely orientated to allow bimolecular radical reaction to proceed. Despite this, radical transfer remains favoured. The effective local concentration of monomer in the micellar state approaches that of the bulk state, and this simple concentration (rather than orientation) factor is probably most important in allowing polymerization.

The rate of exchange of monomer surfactant between micelles is much faster than the rate of oligomer propagation and so a topochemical polymerization of a micelle is extremely unlikely, i.e. the occurrence of 'polymerized micelles' can be discounted. However, oligomeric species can be formed which display micellar-like physical properties and these show a great tendency to aggregate into large units and, indeed, to phase separate.

(Keywords: polymerization; micelle-forming monomers; polymerized micelles)

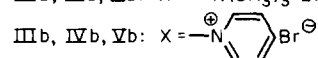
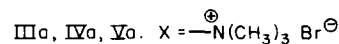
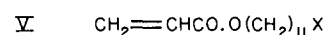
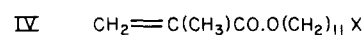
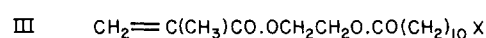
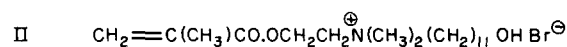
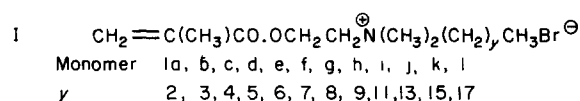
INTRODUCTION

Although potassium styryl undecanoate was synthesized by Freedman *et al.*¹ in 1958 and the 'polysoap' properties of its copolymers examined², the first premediated synthesis and attempted micellar polymerization of an amphiphilic monomer reported in the open literature appears to be the work of Hyde and Robb^{3,4}. They synthesized undecenyltrimethylammonium bromide and sodium undecenyl sulphate and tried to polymerize these and sodium oleate above their critical micelle concentrations (c.m.c.) in order to produce stabilized micelles. Their hope was that such macromolecules might be characterized by light scattering more easily and more quantitatively than normal dynamic micellar aggregates. Since then, the aggregation behaviour in water of vinylpyridinium and vinylimidazolium salts has been investigated, along with their polymerization phenomena⁵⁻¹⁴. Even apparently non-surface-active monomers such as *N*-methylvinylpyridinium methyl sulphate, as well as unambiguously surface-active long-chain alkyl analogues, display an anomalous increase in their spontaneous polymerization rates in water above some critical monomer concentration⁵. The explanation

for this is still a matter for debate¹⁴.

Studies on sodium 10-undecanoate^{15,16} and allyldimethyldodecylammonium bromide¹⁷ have also been reported. These unsaturated molecules would not normally be regarded as particularly active with regard to vinyl propagation (see 'Discussion'). In contrast the sodium 11-methacrylamido undecanoates and related methacrylamido nonionic amphiphiles described by Elias^{18,19} might be regarded as particularly suitable for polymerization in a micellar state. A similar acrylamido undecanoate has been used in the polymerization of water in oil microemulsions²⁰, while the synthesis of acrylamido long-chain sulphonates and benzene-sulphonates and their use in emulsion polymerizations has also been reported²¹.

We have already described our preliminary work²² on a range of amphiphilic (meth)acrylate quaternary ammonium and carboxylate salts, along with two nonionic amphiphilic methacrylate monomers. Most recently a Japanese group has disclosed their work on long-chain alkyl salts of *N,N*-dimethylaminoethyl methacrylate²³ (DMAEMA), and this has prompted us to report our findings with a much wider range of these and related amphiphilic monomers, I-V.



EXPERIMENTAL RESULTS

Materials

In general these were standard laboratory reagents and were used as supplied. The initiators 2,2-dimethoxy-2-phenylacetophenone (DMPAP) and potassium persulphate, $\text{K}_2\text{S}_2\text{O}_8$, were also used without further purification, though azobisisobutyronitrile (AIBN) was recrystallized twice from dry methanol. The monomers were synthesized and their micellization behaviour characterized as described in Part 1 of this work²⁴ (previous paper).

Polymerization of amphiphilic monomers

Photochemically initiated reactions. A known weight of amphiphilic monomer and the appropriate weight of initiator (usually 1 wt %) were introduced into a soda glass graduated flask, and the solution made up to the mark using the appropriate solvent (normally water or an alcohol). The flask was stoppered and the mixture was well shaken to ensure uniform dissolution or dispersion of the components. The initiator 2,2-dimethoxy-2-phenylacetophenone (DMPAP) is only very slightly soluble in water but appeared to be well solubilized in micellar solutions. When large weights were involved, however, some did remain insoluble. Each solution was placed in front of (~ 50 cm) either a high-pressure mercury ultra-violet lamp (200 W) or a tungsten visible lamp (1250 W) for 3 h. No attempt was made to thermostat these reactions. During irradiation the solutions became increasingly opaque, especially those containing amphiphiles at concentrations above their c.m.c. In some cases the polymeric (oligomeric) product

phase separated and eventually sedimented. With aqueous solutions of amphiphiles below their c.m.c. and with the alcoholic solutions no significant change was observed.

After irradiation the total contents of each flask were transferred to a small round-bottomed flask and the products freeze-dried under vacuum at $\sim 10^{-4}$ mmHg. A sample of each product was then submitted for ^1H n.m.r. analysis and molecular weight determination. The solubility characteristics of each were also ascertained (Tables 1, 2, 3 and 5).

Thermally initiated reactions. In these the monomeric amphiphile and initiator (usually AIBN, 1 wt %) were added to a small round-bottomed flask with the required amount of solvent (water or an alcohol). The flask was stoppered and after thorough shaking each mixture was maintained at 80°C for two days. As before the product was isolated by freeze-drying and each was characterized by its ^1H n.m.r. spectrum and molecular weight (Tables 2 and 3).

Photochemically initiated reactions in aqueous solutions of long-chain alcohols. Aqueous solutions of monomeric amphiphiles were prepared just above their c.m.c. values in soda glass graduated flasks. A long-chain alcohol was then added in a molar ratio of 1:1, relative to the amphiphile. DMPAP (1 %) was introduced and the whole mixture shaken vigorously. A thick opaque liquid-crystalline mass was formed in each case, and this was irradiated with visible light as before. Prior to freeze-drying of the product, each was extracted with diethyl ether to remove the long-chain alcohol. The results are summarized in Table 4.

Polymer yields

Quantification of the conversion of amphiphilic monomer to polymer (oligomer) was difficult because of the small quantities involved and the very dilute solutions in the case of systems below their c.m.c. With the ^1H n.m.r. instrumentation routinely available to us (Perkin-Elmer R32, 90 MHz) and because of the low abundance of the vinyl protons relative to the methylene groups, it was possible to obtain only an order of magnitude indication with respect to the yield of polymer (Tables 1-4). Generally for high yields the vinyl protons (and the methacryl methyl group when appropriate) were superficially completely absent, and the remaining resonances (other than the long-chain methylene group) were broadened. The product in this case was generally a fluffy solid. For low yields the ^1H n.m.r. spectrum

Table 1 Photochemical initiation of polymerization of Ik in water^a

| H_2O (ml) | Monomer (g) | [Monomer] relative to c.m.c. | Initiator type ($\text{g} \times 10^3$) | Light source | Product | |
|------------------------------|----------------|------------------------------------|-------------------------------------------------|-----------------|----------|-------------------------|
| | | | | | Yield | [Mol. wt.] ^b |
| 50 | 0.01 | well below | DMPAP (0.1) | visible | ~ 0 | — |
| 100 | 0.05 | below | DMPAP (0.5) | visible | ~ 0 | — |
| 25 | 0.1 | just above | DMPAP (0.5) | visible | low | 2000 |
| 25 | 0.1 | just above | DMPAP (1.0) | ultra-violet | high | 8650 |
| 25 | 0.1 | just above | DMPAP (1.0) | visible | high | 8800 |
| 25 | 0.1 | just above | AIBN (1.0) | visible | high | 5400 |
| 10 | 0.1 | above | DMPAP (1.0) | visible | high | 7750 |
| 25 | 0.25 | well above | AIBN (3.0) | visible | high | 11100 |

^a See 'Experimental' section for details

^b Determined using CHCl_3 solutions

Table 2 Thermally and photochemically initiated polymerizations of monomers Ie-I and II in water^a

| H ₂ O (ml) | Monomer (g) | [Monomer] relative to c.m.c. | Initiator type (g × 10 ²) | Method of initiation | Product | |
|-----------------------|-------------|------------------------------|---------------------------------------|----------------------|---------|--------------------|
| | | | | | Yield | Mol. wt |
| 50 | If (0.1) | below | DMPAP (1.0) | visible | ~ 0 | — |
| 50 | (1.0) | just above | (1.0) | irradiation | high | 1350 ^b |
| 50 | (3.7) | above | (3.7) | | high | 4500 ^b |
| 50 | Ii (0.05) | below | DMPAP (0.05) | visible | ~ 0 | — |
| 50 | (0.10) | just above | (0.10) | irradiation | medium | 2550 ^c |
| 50 | (1.21) | above | (1.2) | | high | 10950 ^c |
| 50 | II (0.05) | just above | DMPAP (0.05) | visible | high | 1950 ^c |
| 50 | (0.10) | above | (0.10) | irradiation | high | 2650 ^c |
| 50 | (0.43) | above | (0.43) | | high | 3050 ^c |
| 50 | II (0.05) | below | DMPAP (0.05) | visible | ~ 0 | — |
| 50 | (0.02) | just above | (0.4) | irradiation | medium | 875 ^b |
| 50 | (1.14) | above | (2.0) | | high | 1100 ^b |
| 25 | Ie (5.9) | above | DMPAP (6.0) | | high | 1475 ^b |
| 25 | Ig (1.4) | above | (1.4) | visible | high | 10350 ^c |
| 25 | Ih (1.0) | above | (1.0) | irradiation | high | 8950 ^c |
| 50 | Ij (0.4) | above | (0.4) | | high | 2650 ^c |
| 25 | If (1.0) | above | AIBN (1.0) | thermal | medium | 575 ^b |
| 25 | Ii (1.0) | above | AIBN (1.0) | | high | 2850 ^c |
| 25 | Ik (1.0) | above | AIBN (1.0) | | high | 1850 ^c |
| 25 | II (1.0) | above | AIBN (1.0) | | medium | 575 ^c |

^aSee 'Experimental' section for details^bUsing CH₃OH solutions^cUsing CHCl₃ solutions**Table 3** Polymerization of monomers If, Ii, Ik, II and II in isotropic alcohol solutions^a

| Monomer (g) | Alcohol (ml) | Initiator type (g × 10 ²) | Method of initiation | Product | |
|-------------|---------------------------------------|-----------------------------------------------------|----------------------|---------|-------------------|
| | | | | Yield | Mol. wt |
| If (1.0) | C ₂ H ₅ OH (50) | DMPAP (1.0) | visible irradiation | ~ 0 | — |
| (1.0) | C ₂ H ₅ OH (50) | AIBN (1.0) | visible irradiation | ~ 0 | — |
| (1.0) | C ₃ H ₇ OH (50) | AIBN (1.0) | thermal | high | — ^c |
| (1.0) | C ₄ H ₉ OH (50) | AIBN (1.0) | thermal | high | — ^c |
| Ii (1.0) | C ₂ H ₅ OH (50) | DMPAP (1.0) | visible irradiation | ~ 0 | — |
| (1.0) | CH ₃ OH (50) | AIBN (1.0) | thermal | medium | 1350 ^b |
| (1.0) | C ₂ H ₅ OH (50) | AIBN (1.0) | thermal | medium | 550 ^b |
| (1.0) | C ₄ H ₉ OH (50) | AIBN (1.0) | thermal | high | 900 ^b |
| Ik (0.1) | CHCl ₃ (25) | DMPAP (0.1) | u.v. irradiation | ~ 0 | — |
| (0.1) | C ₂ H ₅ OH (25) | DMPAP (0.1) | visible irradiation | high | 1050 ^b |
| (1.0) | C ₂ H ₅ OH (50) | AIBN (1.0) | u.v. irradiation | high | 3200 ^b |
| (1.0) | C ₂ H ₅ OH (50) | DMPAP (1.0) | visible irradiation | medium | 3200 ^b |
| (1.0) | C ₂ H ₅ OH (50) | AIBN (1.0) | thermal | high | 2700 ^b |
| II (1.0) | C ₂ H ₅ OH (50) | DMPAP (1.0) | visible irradiation | medium | 2750 ^b |
| (1.0) | C ₂ H ₅ OH (50) | AIBN (1.0) | visible irradiation | medium | 900 ^b |
| (1.0) | C ₂ H ₅ OH (50) | K ₂ S ₂ O ₈ (0.01) | visible irradiation | ~ 0 | — |
| (1.0) | C ₃ H ₇ OH (50) | AIBN (1.0) | thermal | medium | 750 ^b |
| (1.0) | C ₄ H ₉ OH (50) | AIBN (1.0) | thermal | high | 600 ^b |
| II (1.0) | C ₂ H ₅ OH (50) | DMPAP (1.0) | visible irradiation | ~ 0 | — |
| (1.0) | C ₂ H ₅ OH (50) | DMPAP (1.0) | visible irradiation | ~ 0 | — |

^aSee 'Experimental' section for details^bDetermined using CHCl₃ solutions^cSticky product difficult to isolate

corresponded very closely to that of the monomer and it was difficult to tell if any significant quantities of polymer were formed or not. In this case the product was generally a sticky liquid. In a few cases the ¹H n.m.r. spectrum did suggest the presence of a mixture of monomer and polymer and these were judged to be *medium* yields.

Determination of oligomer molecular weights

Since it was deduced quite quickly that high polymer

was not being formed in these polymerizations, it was decided to measure the molecular weight of products by vapour phase osmometry (Hitachi/Perkin-Elmer 115). In order to give a reference point for our measurements, the molecular weight of two polystyrene (Ps) standards were determined using chloroform as the solvent. Since the polar character of our own materials was very different from polystyrene and since methanol was required as the solvent in some cases, and chloroform in others, the molecular weight of monomer Ii also was measured as a

Table 4 Photochemical initiation of polymerization of monomers If, i, k, l, IIIa, IVa and Va as 1:1 mixtures with long-chain alcohols in water^a

| Monomer | Long-chain alcohol | Product | |
|---------|-------------------------------------------------------|---------|-------------------|
| | | Yield | Mol. wt |
| If | CH ₃ (CH ₂) ₇ OH | high | 330 ^b |
| Ii | CH ₃ (CH ₂) ₉ OH | high | 4275 ^c |
| li | CH ₂ =CH(CH ₂) ₉ OH | high | 4425 ^c |
| Ik | CH ₃ (CH ₂) ₁₅ OH | high | 3325 ^c |
| Il | CH ₃ (CH ₃) ₁₇ OH | high | 2200 ^c |
| IIIa | CH ₃ (CH ₂) ₉ OH | high | 500 ^b |
| IVa | CH ₃ (CH ₂) ₉ OH | high | 725 ^b |
| Va | CH ₃ (CH ₂) ₉ OH | high | 500 ^b |

^a See 'Experimental' section for details^b Determined using CH₃OH solutions^c Determined using CHCl₃ solutions

control, using both solvents. The results are given in Table 5.

DISCUSSION

Polymerizations in water

The photochemically initiated polymerization of monomer Ik was studied in most detail. The results in Table 1 show that high yields of oligomer were obtained from solutions of the monomer where the concentration was above the critical micelle value (c.m.c.). For solutions below the c.m.c., conversion to oligomer was virtually zero. No significant difference arose when ultra-violet irradiation was used instead of visible light, and this was confirmed in the case of reactions in isotropic alcohol solutions (Table 3). The initiator, DMPAP, appears therefore to absorb sufficient radiation from a tungsten filament to undergo fission in these systems, although the compound itself is almost white. Furthermore AIBN itself is also sufficiently photoactive. The results in Table 2 confirm that the other micelle-forming monomers in this homologous series, Ie–Il (and also monomer II), behave essentially similarly. Oligomeric species are formed in aqueous solutions where the monomer concentration is above its respective c.m.c., whereas little reaction occurs with solutions below their c.m.c. values. This confirms earlier reports^{12,15,17} using similar amphiphilic monomers and other results^{16,23} which imply that polymerization below the c.m.c. of the monomer is inefficient. We have no data with respect to the kinetics of polymerization in the micelle but we have no evidence to suggest that it is usually rapid. Nagai *et al.*²³ have shown relatively fast reactions using much larger initiator concentrations than we have used (factor ~ 4), though the conversions level off somewhat strangely at ~ 60%. Their reactions in benzene solutions, however, appear to produce ~ 100% conversion in < 15 min and in this case some special phenomenon appears to be operating.

With monomers I and II, it is tempting to suggest that the proximity of the positive nitrogen atom to the active double bond might normally inhibit the close approach of a monomer molecule to the propagating radical, and furthermore that orientation of monomers in a micelle overcomes this effect and facilitates propagation. Acceleration of polymerization as a result of such orientation has been invoked before^{5,7}, and indeed it has

been argued that this effect allows the polymerization of species, such as monoallyl derivatives¹⁷, which normally are inactive in isotropic media²⁵. With monomers such as vinylimidazolium and vinylpyridinium salts, where the positive charge is delocalized, polymerization in isotropic conditions seems easier⁸. In this work the non-micelle-forming members of the homologous series, Ia–d, also showed a reluctance to polymerize in isotropic aqueous solutions, and this tends to confirm the charge repulsion idea. However, the micelle-forming monomers, III–V, with the polymerizable group remote from the quaternary ammonium nitrogen, though studied in less detail, displayed essentially the same behaviour as Ie–l; i.e. when aqueous monomer solutions with concentrations above their c.m.c. values containing 1 wt% of DMPAP were irradiated in the usual way, a high yield of oligomer was obtained in each case. Similar reactions performed with solutions below their c.m.c. values gave little evidence of polymerization. With these monomers it is difficult to invoke a charge repulsion phenomenon alone as inhibiting polymerization, since the charge and the vinyl group are sufficiently remote for each molecule to adopt a conformation quite satisfactory for close approach of the incoming monomer to the propagating radical. Furthermore, of course, the metal salts of acrylic and methacrylic acids polymerize quite readily in aqueous isotropic solution²⁶.

What other factors therefore might give rise to a lack of reaction in solutions below their c.m.c. values? First, the actual monomer concentration is very low and on micellization the *local* concentration rises very sharply, indeed to a value which must be close to that of pure molten monomer. Secondly, in the absence of micelles the concentration of initiator present as a true molecular solution will also be very low. Thus in our reactions where we have deliberately taken no particular precautions to exclude oxygen, these factors may simply contribute to produce extremely slow propagation via a low concentration of radicals that are being constantly scavenged by oxygen.

In an attempt to improve the real flux of radicals generated in aqueous solutions, the water-soluble sodium salt of azobisisovaleric acid was used in a few thermally initiated reactions. This indeed produced good yields of a fluffy polymeric product from monomers I. However, this subsequently proved to be the sodium salt of polymethacrylic acid formed by facile hydrolysis of either the monomer or polymer at the high pH of these reactions. Intramolecular interaction of the methacryloxy group in these monomers with the onium nitrogen centre, as postulated in Part 1, would be expected to provide anchimeric assistance in OH[−] ion-catalysed hydrolysis of these molecules (Figure 1). In addition, of course, the pK_a of the conjugate alcohol of the leaving alkoxide is extremely favourable.

Table 5 Molecular weight calibration

| Sample (Mol. wt) | Molecular weight (found) | |
|------------------|--------------------------|----------|
| | Chloroform | Methanol |
| Ps (5000) | 2610 | — |
| Ps (10000) | 6880 | — |
| Ii (406) | 550 | 250 |

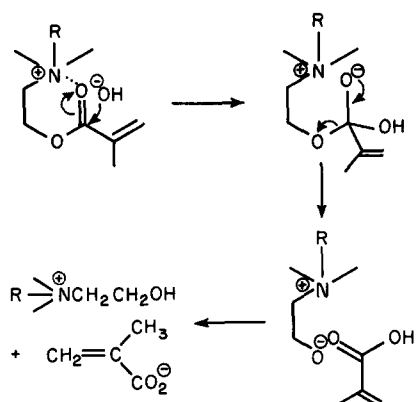


Figure 1 Anchimeric assistance to hydroxide ion hydrolysis of monomers I via intramolecular interaction of the methacryloxy ethyl substituent with the quaternary nitrogen centre

Polymerizations in isotropic alcohol solutions

The results of the polymerizations of monomers If, i, k, l and II in ethanol, n-propanol and n-butanol solutions are summarized in Table 3. In general the monomer concentration employed was low, ~2 wt %, though this was still higher than the nominal concentrations (though not the *local* intramicelle concentrations) used in the aqueous solutions. Somewhat surprisingly the photochemically initiated reactions produced low yields, although in general conversions were very much better with thermal fragmentation of AIBN. In all cases, however, the molecular weight of the products obtained was very low (see later). Fewer experiments were performed with monomers III–V, but again their behaviour seemed essentially the same as I and II. Since these reactions were carried out in the presence of oxygen, then a retarding/inhibiting action cannot be discounted. However, any effect of oxygen here must also be present in the micellized aqueous solutions, where apparently the highly orientated monomer array and very high local monomer concentration more than compensate.

Polymerizations in fatty alcohol lamellae

Molar (1:1) mixtures of ionic surfactants and fatty alcohols in water are known to form a liquid-crystalline lamellae phase²⁷ with dimensions far beyond that of micelles. In this, the fatty alcohol probably acts as a co-amphiphile spacer between charged surfactant molecules. With the addition of shorter-chain alcohols to oil-in-water emulsions stabilized by ionic surfactants, each droplet can assume much greater curvature as a result of the insertion of the short weakly surface-active alcohol into the interface. Thus the emulsion droplet size falls sharply with the formation of a clear microemulsion²⁸. In this work it was thought that the spacing of a polymerizable amphiphile by a fatty alcohol in a lamellae phase might shield the amphiphile charges from each other, and result in rapid propagation to high molecular weight species. In practice, highly viscous opaque liquid-crystalline solutions were obtained prior to polymerization, and the subsequent yield of product was high in each case (Table 4). However, there was no evidence for a sharp rise in the molecular weight and somewhat disappointingly again only oligomers were obtained.

Solubility characteristics of products

The solubility characteristics of monomers and their corresponding oligomers are shown in Table 6. The amphiphilic nature of the monomers shown made them compatible with many organic solvents and only limited data are shown here. The characteristics of the oligomers were very different. All were essentially insoluble in water. During polymerization of clear aqueous solutions, an opaque appearance was slowly generated and in some cases gross phase separation and aggregation occurred, followed by sedimentation (see later). This was most apparent for monomers with high c.m.c. values where the overall weight percentage of material dissolved was larger in order to be in the micellar phase region. Products formed in alcohol solutions generally remained in solution, although after isolation and drying Ij–l would not dissolve in methanol. Even those oligomers which did not phase separate completely from water solutions failed to redisperse in water after they had been dried thoroughly. This behaviour has been recorded before^{1,2,8,12}, even in the case of polymers which appear to be initially fully water-soluble. It seems that in the dry state the ionic groups are tightly bound within a hydrophobic network; indeed they may form microphase-separated domains. These seem to be highly inaccessible to water, although dissolution or swelling with a water-miscible organic solvent can subsequently allow penetration and finally dissolution by water^{1,2}. The solubility of oligomers from Ie–l in methanol and chloroform showed a systematic variation. The oligomer from Ie and f were methanol-soluble but chloroform-insoluble. As the length of the alkyl chain on the monomer segment was increased, this behaviour was reversed, in keeping with the change in hydrophobic/hydrophilic ratio. Oligomers from Ig–i were soluble in both solvents. Those from II–V were insoluble in chloroform. Perhaps somewhat predictably the presence of the hydroxyl group on the end of the alkyl chain in II renders the oligomer insoluble in chloroform, whereas from Table 6 we can predict that the analogous species without this hydrophilic terminus would be soluble in both chloroform and methanol.

Table 6 Solubility characteristics of monomers and corresponding oligomers

| | Monomer | | | Oligomer | | |
|------|-------------------------------|--------------------|-------------------|-------------------------------|--------------------|-------------------|
| | H ₂ O ^a | CH ₃ OH | CHCl ₃ | H ₂ O ^c | CH ₃ OH | CHCl ₃ |
| Ie | + | + | + | – | + | – |
| If | + | + | + | – | + | – |
| Ig | + | + | + | – | + | + |
| Ih | + | + | + | – | + | + |
| Ii | + | + | + | – | + | + |
| Ij | + | + | + | – | – | + |
| Ik | + | + | + | – | – | + |
| Il | + | + | + | – | – | + |
| II | + | + | + | – | + | – |
| IIIa | + | + | + | – | + | – |
| IIIb | + | + | + | – | + | – |
| IVa | + | + | + | – | + | – |
| IVb | + | + | + | – | + | – |
| Va | + | + | + | – | + | – |
| Vb | + | + | + | – | + | – |

^a All display c.m.c. behaviour

^b Needs warming to dissolve even below c.m.c.

^c Ii–l, III–V yielded stable colloidal solutions

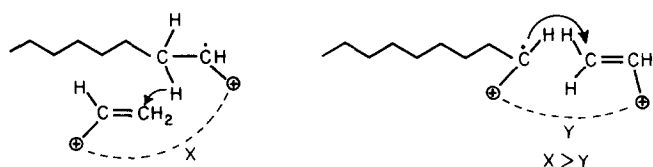


Figure 2 Pictorial representation of the reduced charge repulsion involved in radical transfer to monomer, *versus* that in propagation

Molecular weights of products

As a result of the variation in solubility of the oligomers described above, it was necessary to measure some molecular weights in chloroform and some in methanol solution. Since a colligative method was used, the data obtained are number average, \overline{M}_n , values. The measurements of the molecular weights of three control species show that the values derived from chloroform solutions seem reasonably accurate. However, the value for monomer II in methanol is significantly lower than the real one. This variation must be considered in interpreting some of the data in Tables 2 and 4. A consistent pattern emerges that molecular weights determined from methanol solutions are generally lower than those obtained for species in chloroform solutions, for a given group of polymerization reactions.

The highest molecular weight of any product was $\sim 11\,000$. These values were obtained for oligomers from micellized monomers in aqueous solution (Tables 1 and 2) and were measured in chloroform. They represent, therefore, reasonably accurate estimates of the \overline{M}_n of these species, corresponding to a degree of polymerization \overline{DP}_n of ~ 25 . It might be argued that aggregation of monomers in a micelle might limit the maximum molecular weight achievable (see next section on 'Polymerized micelles'), but in fact the species obtained under all other circumstances in this work were of even lower molecular weight. Indeed \overline{DP}_n values as low as 2–4 were apparent in some cases. This suggests that some other factor is overriding in controlling the degree of polymerization; and a facile radical transfer reaction would indeed be consistent with this result. In a normal free-radical polymerization, propagation is significantly favoured over transfer. However, with these charged monomers it could be that this difference is significantly reduced. Certainly in a crude pictorial representation one can see how radical transfer might be achieved with the positive charges kept further apart than is possible with propagation (Figure 2). However, one could argue similarly for the polymerization of the salts of acrylic and methacrylic acids and there is no evidence of similar behaviour. If transfer reactions do play a major role, however, careful n.m.r. analysis of the oligomers should show structural evidence of this, and we are currently pursuing this.

'Polymerized micelles' and 'self-micellizing polymers'

The original objective of Hyde and Robb³ was to stabilize a micelle by polymerizing it, and likewise our main objective was to produce micellar-sized polymer particles. In the case of polymerizable vesicle-forming monomers, there is good evidence that a topochemical polymerization occurs within each vesicle²⁹. Furthermore, in the case of polymerized unilamellar vesicles, the molecular weight of the isolated polymer is consistent

with the measured size of the original vesicular structure³⁰. Although vesicles are thermodynamically unstable and slowly aggregate, and indeed ultimately phase separate, the kinetics of exchange of the individual amphiphiles comprising the vesicle bilayer are slow. In contrast, micelles are thermodynamically stable, but the kinetics of exchange of individual amphiphilic molecules are fast. The average time taken³¹ for surfactant to leave a micelle varies with the c.m.c. value but is typically 10^{-5} – 10^{-9} s. We have compared these times with the average time taken for a monomer molecule to add to its propagating radical (10^{-2} – 10^{-6} s) and hence concluded that a topochemical reaction to form a 'polymerized micelle' is extremely unlikely³². Hyde and Robb³ solubilized a small amount of styrene and AIBN in hexadecyltrimethylammonium bromide micelles and irradiated the solution. The overall monomer content was very much lower than that in an emulsion polymerization. There were no monomer droplets and each micelle was estimated to contain an average ~ 90 styrene molecules. Polymerization within isolated micelles would therefore yield a maximum molecular weight of ~ 9000 (assuming no transfer and termination). In practice the molecular weight of the product polymer was $\sim 500\,000$! This showed very dramatically either that micelles are fused before polymerization is complete within each, or that rapid transfer of styrene between micelles enables such large molecular weights to be generated. With this in mind, and remembering the much higher molecular solubility of a polymerizable amphiphile in water, relative to that of styrene, again it seems extremely unlikely that a micelle of polymerizable amphiphiles could be united to form a discrete 'polymerized micelle'. Furthermore the detailed conformational differences characterized for monomers I *versus* II–V (see Part I²⁴) would not be anticipated to be significant in the polymerization of these kinetically mobile species. In our reactions the generation of significant opacity indicated clearly the formation of colloidal particulate species of very much bigger dimensions than micelles. Kammer and Elias^{18,19} have obtained electron micrographs of spherical particles produced by 'micellar' polymerization of some amphiphilic acrylamido monomers. These also are of the dimensions of typical emulsion polymerization particles (500–2000 Å diameter) and suggest growth beyond the initial micellar dimensions. Indeed, in some cases our species continued to grow in size, finally phase separating. With the limitation of the molecular weight of the products to a maximum of $\sim 11\,000$, it is tempting to suggest that indeed micelles with an aggregation number of ~ 25 are polymerized in discrete isolation. However, this result is almost certainly fortuitous, arising from facile monomer transfer as described earlier.

The inability to polymerize an individual micelle and maintain its independence does not of course eliminate the possibility of using other routes to produce 'self-micellizing' polymers or oligomers, i.e. species which spontaneously form a micellar structure in water from a single or small group of macromolecules. A number of papers^{1,2,8,16,17,33,34} refer to polymeric species with a 'polysoap' structure forming micelles, such that in effect the c.m.c. is ~ 0 . The evidence for this is indirect and relates for example to the ability of such solutions to solubilize dyes at concentrations approaching zero^{16,17}.

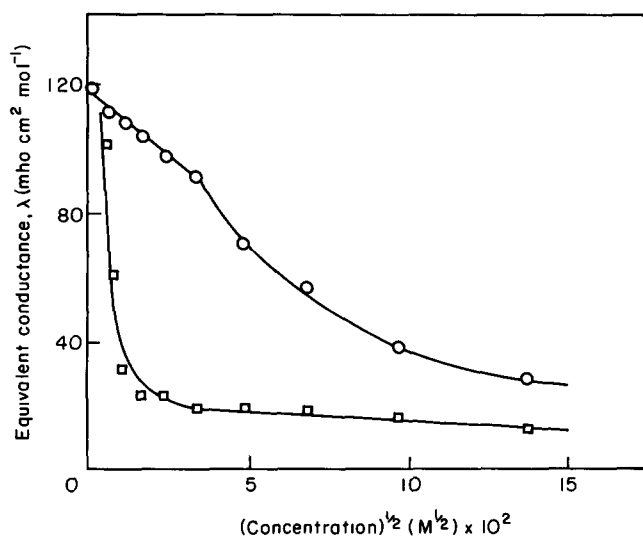


Figure 3 Plots of equivalent conductance versus (concentration)^{1/2} for monomeric species (O) and polymerized species (□) (II-I, III-V)

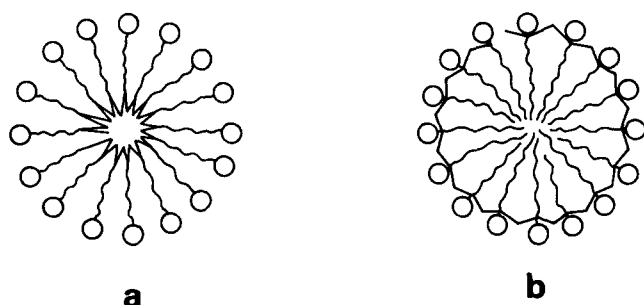


Figure 4 Two-dimensional representation of idealized 'polymerized' micelle in water, formed from an amphiphilic monomer with a polymerizable group: (a) at the tail end, (b) at the head

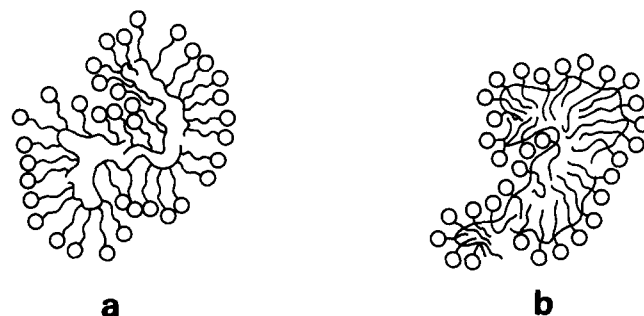


Figure 5 Two-dimensional representation of a more realistic micelle-like aggregate of surface-active oligomers, formed for a polymerizable amphiphilic monomer: (a) and (b) as in Figure 4

and to the apparent disappearance of micellar transitions indicated in conductivity data⁸ obtained down to very low concentrations. In our work, polymerization of monomers II-I and III-V led to opaque solutions without gross phase separation, and using these solutions the conductivity and dye solubilization behaviour was examined over a concentration range extending far below the original c.m.c. values. As with earlier work we also detect dye solubilization below the original c.m.c. and a complete change in the shape of the equivalent conductivity versus (concentration)^{1/2} plots (Figure 3). This indeed shows a loss of the micellar transition, but the conductivity behaviour becomes dominated by the

polyelectrolyte nature of the system³⁵, and no firm conclusion about the 'polysoap' or micellar nature of these solutions can be drawn from these data.

If the term 'micelle' applied to a polymeric or oligomeric molecule with a 'polysoap' structure implies the formation of a small relatively symmetric species (Figure 4) in water analogous to a soap micelle, with a c.m.c. = 0, then this is almost certainly misrepresentative. On the other hand, if it simply conveys that one or a small number of molecules adopts a conformation such that a discrete hydrophobic environment is formed within the molecule(s) (Figure 5), then this is almost certainly much closer to reality. Such a structure would allow, for example, the solubilization in water of oil-soluble species and other micelle-like properties for virtually all finite concentrations. With our materials, as the overall concentration of polymeric/oligomeric molecules rises, then the tendency to aggregate into increasingly larger units is high, certainly higher than that exhibited by small amphiphilic molecules. The window between colloidal independence and aggregation and phase separation appears to be very much lower. In designing oligomeric surfactants to function at higher concentrations, this factor will have to be considered and suitable structures will almost certainly have to have a higher overall hydrophilicity. This might be achieved by reducing the length of alkyl chains below that normally thought of as being necessary for micellization to occur, or alternatively increasing the average number of ionic groups per conventional alkyl chain. Clearly these species have unusual properties and their importance and application will grow. Much more work is needed in terms of synthesis, and the evaluation of physical properties at higher concentrations in water, in the case of those species which do not phase separate. This will improve considerably our predictive capabilities in terms of designing polymeric amphiphiles for particular applications.

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