Photopolymerization of Micelle-Forming Monomers. 2. Kinetic Study and Mechanism

Didier Cochin, Raoul Zana, and Françoise Candau*

Institut Charles Sadron (CRM-EAHP),
CNRS-ULP Strasbourg, 6, rue Boussingault, 67083 Strasbourg Cédex, France

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ABSTRACT: The kinetics of the photoinitiated polymerization of aqueous micellar solutions of *n*-alkyldimethyl(vinylbenzyl)ammonium chloride surfactants (C*n*-STY with $n = 8$ and 16) have been investigated. The rate of polymerization was determined by dilatometry and was found to be proportional to the first power of the monomer concentration, [M], and to the half-power of the oil-soluble initiator concentration, [I]. A dependence of the polymer molecular weight on $[I]^{-0.6}$ was observed. These scaling laws are close to those obtained for styrene emulsion polymerization. A mechanism is proposed and discussed in terms of micellar dynamics. Initiation occurs within the micelles, and the polymerizing micelles are fed monomeric surfactants coming from noninitiated micelles by diffusion through the aqueous phase. Different situations are discussed depending upon the degree of reactivity of the polymerizable group, the micelle lifetime, and the fraction of micellized surfactant with respect to that of free surfactant. This general mechanism accounts for the above data as well as for other results reported in the literature. It is concluded that a topological polymerization within a micelle is highly improbable.

Introduction

Several studies have recently been devoted to the polymerization of micelle-forming monomers above their critical micelle concentration.[1–14] Research in this field had several objectives. The first objective was to fix permanently these labile systems in order to get a better description of their structures.[15] The second objective was based on the expectation that covalently stabilized micelles should be more appropriate for technological applications than their unpolymerized counterparts.[16] Besides, micellar polymerization may offer a new way to prepare polymers not easily obtainable in isotropic solutions (due to their low reactivity), as in the case for sodium 10-undecenoate[17] or allyldimethyldodecylammonium bromide.[18] Eventually, polymerizable surfactants may be used for latex stabilization by preventing surfactant desorption from the particle surface.[19–21]

However, from the various studies performed so far, it is hard to draw definite conclusions regarding the mechanism of micellar polymerization and the characteristics of the polymers thus produced. Indeed the data are often conflicting, rather fragmentary, and dealing mainly with only one of the many problems raised by this process, such as the effect of the polymerizable group on the micelle characteristics or the effect of the micellar structure on the kinetics and polymerization mechanism or the structure of the polymerized particles.

In this paper and the preceding one (part 1[22]), we have attempted to gain further insight into these various aspects by a thorough study of the polymerization of cationic micelles formed from alkyldimethyl(vinylbenzyl)ammonium chlorides (C*n*-STY with $n = 8$ and 16). Part 1[22] described the characteristics of the aqueous micellar solutions before and after polymerization. The use of several complementary techniques provided significant information on the structure of the polymerized particles. This structure is essentially controlled by the length of the alkyl chain of the surfactant. The polymers formed from C16-STY surfactants exhibit a structure similar to that of a polysoap with intramolecular hydrophobic microdomains while poly(C8-STY) behaves like a classical polyelectrolyte. All the polymers were shown to have high molecular weights (3×10^5–3×10^6), clear evidence that the initial micellar structure is not preserved upon polymerization.

In order to get a more complete picture of the events occurring during the micellar polymerization of C*n*-STY, we have undertaken an investigation of the kinetics and of the mechanism of polymerization of the micelles formed from C*n*-STY surfactants. We present below the results of experiments designed to determine the role of monomer and initiator concentrations on the rate and degree of polymerization. On the basis of these results, we propose a general mechanism which attempts to reconcile the various and often conflicting conclusions previously reported. In particular, the question regarding the possibility of a topological polymerization, that is, a polymerization of the individual micelles (without changes of dimensions and molecular weights), is discussed. It is shown that such a polymerization is very unlikely. The calculation is based on a comparison between the average time for the addition of a monomer to a growing radical and the mean lifetime of a micelle throughout the polymerization. The time over which the whole micelle persists as an entity is indeed the relevant parameter to be taken into account here rather than the mean residence time of a unimer in a micelle, as often considered in literature reports.

Experimental Section

Materials. Surface-Active Monomers. The synthesis of the alkyldimethyl(vinylbenzyl)ammonium chlorides, referred to as C*n*-STY ($n = 8$ and 16) has been described in part 1.[22]

Photoinitiator. α,α-Dimethoxy-α-phenylacetophenone (DMPA) was used as received (Aldrich). This compound is only slightly soluble in water (2.5×10^{-4} mol/L) but is easily solubilized in micellar solutions. Its reactivity is enhanced with respect to other benzoin ethers containing only one methoxy group, as the presence of another methoxy group induces a second fragmen-

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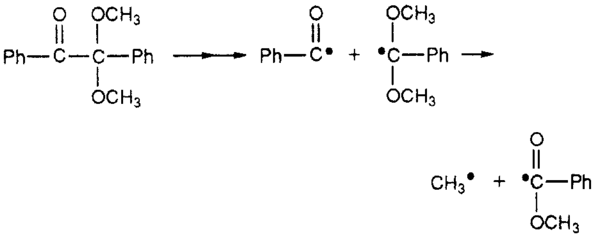
Table I. Volume Contraction Factors for C8-STY and C16-STY Monomers

	$10^5 f_c$ (mol/mm)	
monomer	UV spectrophotometry	gravimetry
C8-STY	5.22	6.1
C16-STY	3.65	3.85

tation of the substituted benzylic radical according to



$$\mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}{-}Ph \longrightarrow Ph{-}\overset{\overset{O}{\|}}{C}\bullet + \bullet\underset{\underset{OCH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}{-}Ph \longrightarrow CH_3\bullet + \bullet\underset{\underset{OCH_3}{|}}{\overset{\overset{O}{\|}}{C}}{-}Ph} \quad (1)$$

The benzoyl radical is primarily responsible for the initiation.[23]

Polymerization Procedure. Polymerization rates were determined dilatometrically. The azobis(isobutyronitrile) used as initiator in the experiments reported in part 1[22] was not appropriate for the dilatometric technique because it gives rise to nitrogen bubbles upon decomposition, and it was replaced by DMPA. Purified nitrogen was bubbled in the dilatometer containing the aqueous micellar solutions under stirring for about 30 min to eliminate oxygen, before irradiation at 20 °C by a source of ultraviolet light.

The dilatomer consisted of a cylindrical Pyrex cell of 3-cm depth and 4-cm diameter. Except for its front side, the cell was enclosed in a glass jacket which allowed an efficient temperature control. It was fitted with two ground-glass joints; one for filling it and inserting a thermocouple and the other for mounting a graduated (1-mm increments) capillary column with an inner diameter of 1 mm. The light source was a Hanovia XBO mercury vapor–xenon lamp. A first lens collimated the light from the source, sending it through a 10% copper sulfate filter with a 5-cm light path used to absorb infrared radiation and prevent heating of the cell and a Zeiss neutral density filter used to attenuate the light intensity. A second lens set after the filters formed a parallel light beam. At last, a diaphragm, of aperture D variable between 5 and 50 mm, was placed in front of the cell to control the intensity of the incident beam. Wavelengths lower than 300 nm were cut off, and the light intensity was maximum at 360–370 nm.

Determination of the Volume Contraction Factor Associated to the Polymerization. The knowledge of the volume contraction factor, f_c, which is a characteristic of the polymerization reaction allows the determination of the rate of polymerization.[24] This factor was evaluated by gravimetry and by UV spectroscopy. Its values expressed in moles of polymerized monomer per millimeter of contraction in the capillary are listed in Table I. They are close to those reported for other vinyl monomers.[25] In the following, the conversion–time curves were determined using the f_c values obtained by gravimetry, as they are somewhat more accurate.

Temperature Control. To correct the dilatometric data collected during the experiment for the effect of the heat released by the polymerization reaction, the variation of temperature with time was first recorded during the polymerization of a C8-STY solution for two different light intensities corresponding to two different diaphragm openings. During the first few minutes, the temperature rose rapidly and then it began to fall and the rate of reaction decreased. The temperature rise did not exceed 0.4 °C.

In a second step, the change of the solution level in the capillary with temperature was measured for the same C8-STY solution but in the absence of DMPA (no polymerization). This allowed us to correct the dilatometric data recorded during polymerization for the heat released by this reaction. Table II shows the impact of this effect on two representative values of the polymerization rate R_p. The relative errors on R_p are small. Alternatively, one can reduce the rate of polymerization by varying the aperture of the diaphragm, making corrections for temperature unnecessary. This last procedure has been retained for the kinetic experiments.

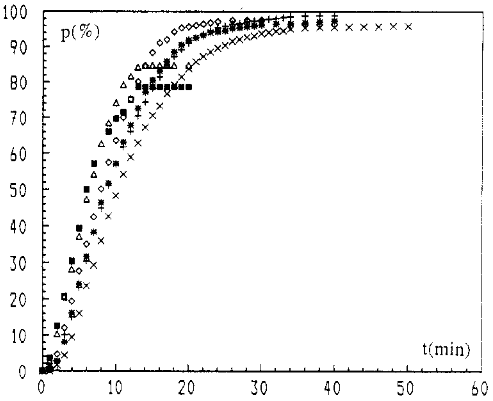


Figure 1. Variation of the degree of conversion, p, with time for different C16-STY concentrations (mol/L). (×) 9.66×10^{-2}; (+) 6.66×10^{-2}; (*) 4.79×10^{-2}; (◇) 3.49×10^{-2}; (■) 2.52×10^{-2}; (△) 1.80×10^{-2}; [DMPA] = 3.9×10^{-5} M.

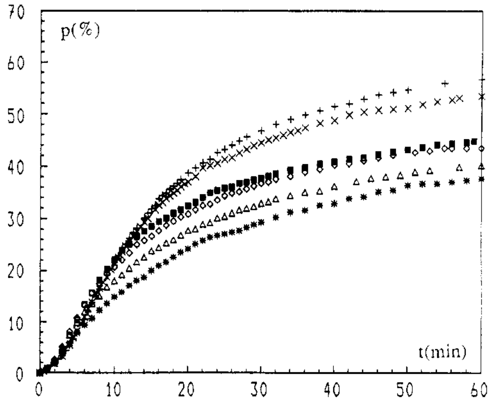


Figure 2. Variation of the degree of conversion, p, with time for different C8-STY concentrations (mol/L). (+) 0.200; (×) 0.180; (■) 0.140; (◇) 0.120; (△) 0.106; (*) 0.100; [DMPA] = 1.95×10^{-4} M.

Table II. Maximum Temperature Rise and Relative Error on R_p in the Polymerization of C8-STY

$10^4 R_p$ (M s^{-1})	max temp rise (°C)	relative error on R_p (%)
2.57	0.4	4
1.63	0.35	0.43

Results

The kinetic studies examined the influence of the monomer and initiator concentrations (C and [I], respectively) on the rate and degree of polymerization.

1. Rate Dependence on Monomer Concentration. The experiments were performed on solutions of increasing initial surfactant concentration, above the cmc, and constant [I]. In Figures 1–3 are reported the degree of conversion p versus time (t) curves for C16-STY and C8-STY. p increases almost linearly with time after a short induction period likely due to traces of oxygen or impurities and then levels off at higher p.

For C16-STY, the curves approach asymptotically complete conversion within 15–30 min; the lower the initial surfactant concentration, the faster a quantitative yield is reached.

In the case of C8-STY, high degrees of conversion (>90%) are reached after longer times, usually a few hours, as shown in Figures 2 and 3. These results are directly related to the polymerization mechanism (see the Discussion section).

The rate of polymerization, R_p, was calculated from the slope of the linear part of the p versus t plots in Figures

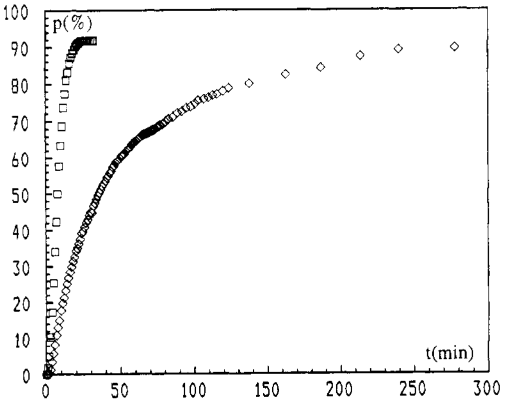


Figure 3. Variation of the degree of conversion with time for C16-STY (□) and C8-STY (◇) at $C = 0.1$ M.

Table III. Polymerization Rates and Fraction of C16-STY Micelles Containing One Initiator Molecule at Different Surfactant Concentrations ([I] = 3.90 × 10⁻⁵M; Diaphragm Aperture *D* = 2.5 cm)

10^2C (M)	n	10^5R_p (M s^{-1})
1.80	0.147	2.67
2.52	0.108	3.47
3.49	0.080	4.45
4.79	0.062	5.48
6.66	0.056	7.69
9.66	0.041	10.58

Table IV. Polymerization Rates and Fraction of C8-STY Micelles Containing One Initiator Molecule at Different Surfactant Concentrations ([I] = 1.95 × 10⁻⁴ M; Diaphragm Aperture *D* = 2.5 cm)

C (M)	n	10^5R_p (M s^{-1})
0.100	0.130	4.58
0.106	0.108	6.96
0.120	0.078	9.44
0.140	0.055	11.10
0.180	0.035	13.30
0.200	0.030	15.13

Table V. Cmc Values of the Surfactants in the Presence of DMPA

surfactant	10^4[DMPA] (mol·L^{-1})	cmc (mol·L^{-1})
C8-STY	1.95	0.07 (0.08)[a]
C16-STY	0.39	2.6×10^{-4} (2.9×10^{-4})[a]

[a] The values in brackets were obtained in the absence of initiator.

1 and 2. The values of R_p are reported in Tables III and IV together with the fraction n of micelles containing one initiator molecule at the start of the polymerization calculated from the equation

$$n = N[\mathrm{I}]/(C - \mathrm{cmc}) \qquad (2)$$

where N is the micelle aggregation number. N was determined by time-resolved fluorescence quenching for C16-STY[22] and taken as 20 for C8-STY (cf. the preceding paper). This assumption finds its justification in the N values reported for similar surfactants, as, for example, potassium octanoate.[26,27] Besides, we have checked by conductivity experiments that the cmc values of the surfactants were not much affected by the presence of DMPA in the micellar solutions (Table V).

The values of n indicate that few micelles contain one initiator molecule (1 per 7–30 micelles depending on the concentration range investigated). This value corresponds to the initial surfactant solution and is subject to variations upon polymerization.

Figures 4 and 5 represent the plots of log R_p versus log C for the two surfactants. Least-squares fits of the linear part of the curves yield the relationships

$$R_p \propto C^{0.82} \quad \text{for C16-STY}$$
$$R_p \propto C^{0.90} \quad \text{for C8-STY} \qquad (3)$$

The unusual shape of the plot for C8-STY can be interpreted as follows. When decreasing C to values close to the cmc, the fraction of micellized monomer becomes much lower than that of free surfactant, leading to the observed drop of the polymerization rate. Indeed, as discussed below, the polymerization rate is much larger for micellized monomer than for free surfactant. The presence of a large amount of free surfactant in the aqueous phase of the C8-STY *initial* solutions is also likely to be responsible for the lower reaction rates observed at the *end* of the polymerization.

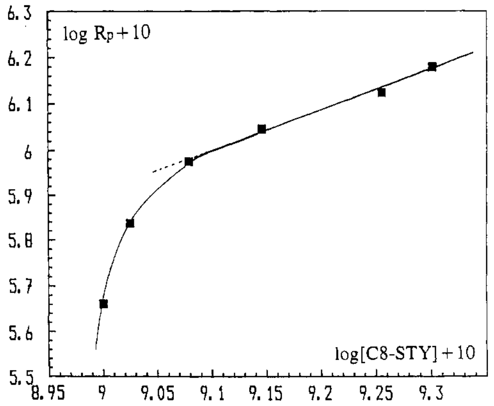


Figure 4. Dependence of the polymerization rate of C8-STY on concentration [DMPA] = 1.95 × 10⁻⁴ M.

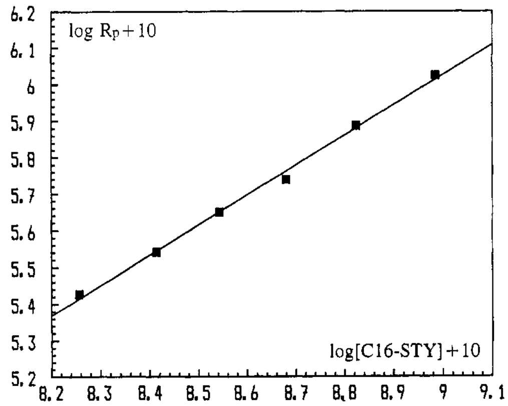


Figure 5. Dependence of the polymerization rate of C16-STY on concentration [DMPA] = 3.90 × 10⁻⁵ M.

Table VI. Fraction of C16-STY Micelles Containing One Initiator Molecule, Rate of Polymerization, and Polymer Molecular Weight for Different DMPA Concentrations (*C* = 4.73 × 10⁻² M; Diaphragm Aperture *D* = 2.5 cm)

10^5[DMPA] (M)	n[a]	10^5R_p (M s^{-1})	$10^6\bar{M}_w$
1.00	0.016	2.94	3.29
1.50	0.024	3.47	2.64
2.30	0.037	4.38	2.15
3.51	0.057	5.48	1.73
5.03	0.082	6.95	1.16
7.25	0.118	7.55	0.93

[a] Calculated using the N values reported in part 1.

2. Rate Dependence on Initiator Concentration. The values of R_p obtained by varying the initiator concentration at constant monomer content are reported in Tables VI and VII together with the values of n and of the polymer weight-average molecular weight, $\bar{M}_w$, determined by static light scattering (see part 1[22]). Notice

Table VII. Fraction of C8-STY Micelles Containing One Initiator Molecule, Rate of Polymerization, and Polymer Molecular Weight for Different DMPA Concentrations (C = 0.16 M; Diaphragm Aperture D = 2.5 cm)

10^4[DMPA] (M)	n^a	$10^5 R_p$ (M s^{-1})	$10^5 \bar{M}_w$
0.72	0.016	5.34	8.15
1.11	0.025	6.30	6.15
1.89	0.042	8.27	4.63
3.80	0.084	10.20	2.63
7.61	0.169	11.70	2.04

[a] Calculated using N = 20.

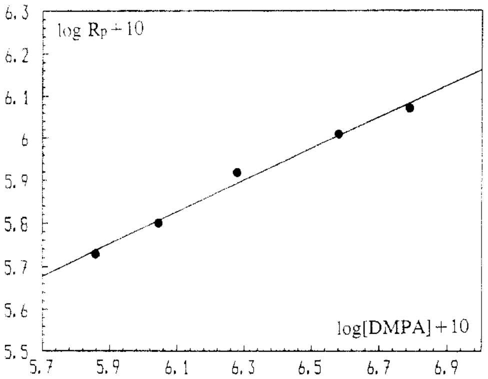


Figure 6. Dependence of the polymerization rate of C8-STY solution on the initiator concentration. [C8-STY] = 0.16 M.

again the small fraction of micelles containing one initiator molecule (1 per 6–60 micelles depending on the conditions).

The following relationships were obtained for the effect of initiator concentration on the polymerization rate.

$$R_p \propto [I]^a \qquad (4)$$

with a = 0.38 for C8-STY (see Figure 6) and a = 0.50 for C16-STY (plot not shown).

In the case of C16-STY, the finding of a polymerization rate proportional to the square root of the initiator concentration is a classical result in free-radical polymerization.[24] The order 0.38 obtained for C8-STY can be ascribed to the fact that part of the light intensity is absorbed by the reaction medium due to the presence of residual impurities difficult to remove from this short alkyl chain compound.

To check this point, we have measured R_p as a function of the relative light intensity, I_r. Indeed, in the absence of any side-chain reaction, one expects similar scaling laws for the variations of R_p with I_r and [I].[24] The rate of polymerization was measured for different values of the diameter D of the diaphragm aperture and was found to vary as $D^{0.99}$ (Figure 7). As I_r is proportional to the area of the parallel light beam incident on the cell, one has $R_p \propto I_r^{0.49}$. This finding supports our assignment of the $[I]^{0.38}$ dependence of R_p for C8-STY to some impurities present in this compound.

3. Molecular Weight Dependence on Initiator Concentration. The molecular weight dependence on the initiator concentration was found to obey the relationship:

$$\bar{M}_w \propto [I]^{-b} \qquad (5)$$

with b = 0.61 for C8-STY (see Figure 8) and b = 0.64 for C16-STY (plot not shown).

From the set of results presented above, we can draw the following conclusions:

(i) A good agreement is observed between the scaling laws obtained for the two polymerizable surfactants.

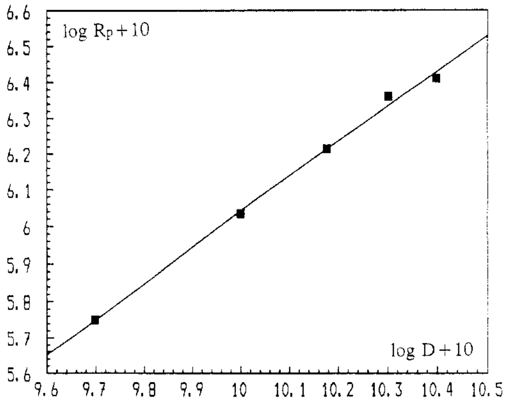


Figure 7. Dependence on the polymerization rate on the diaphragm aperture diameter (in cm). [C8-STY] = 0.16 M; [DMPA] = 1.95 × 10^{-4} M.

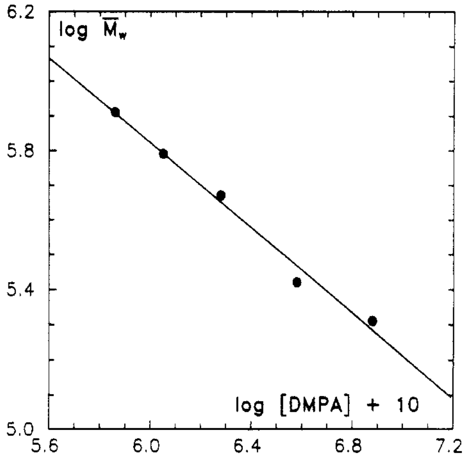


Figure 8. Dependence of the polymer molecular weight obtained upon polymerization of C8-STY solutions on the initiator concentration.

(ii) Polymerization kinetics close to first order with respect to monomer and half-order with respect to initiator as well as a dependence of molecular weight on $[I]^{-0.6}$ agree fairly well with data reported in literature for other polymerizable surfactants, both nonionic[11] and anionic.[4,28,29] In addition, our kinetic data are close to those obtained for styrene emulsion polymerization ($R_p \propto [M][I]^{0.4}$ and DP $\propto [I]^{-0.6}$, Smith–Ewart case 2).[24]

4. Determination of the Overall Activation Energy. The C8-STY and C16-STY micellar solutions were polymerized photochemically at temperatures ranging from 10 to 30 °C. Experiments could not be conducted at higher temperatures because of the desorption of the nitrogen dissolved in the micellar solutions during bubbling.

We first checked that no spontaneous polymerization occurred in the absence of UV irradiation in the T range investigated. This is an indication that there is no thermal contribution to the polymerization. The initial rates of polymerization measured at various temperatures are plotted in Figure 9 according to the Arrhenius equation:[24]

$$\ln R_p = B - E/RT \qquad (6)$$

where B is a constant which depends on [I] and C. The overall activation energy E is equal to $E_p - E_t/2$, E_p and E_t being the activation energies of the propagation and termination steps, respectively.

The plots are linear and yield $E_{\text{C8-STY}}$ = 30.1 kJ/mol and $E_{\text{C16-STY}}$ = 40.0 kJ/mol. These values are relatively high compared to those observed in photochemical initiation, which are usually on the order of 20 kJ/mol.[24] However, the propagation activation energy of various styryl com-

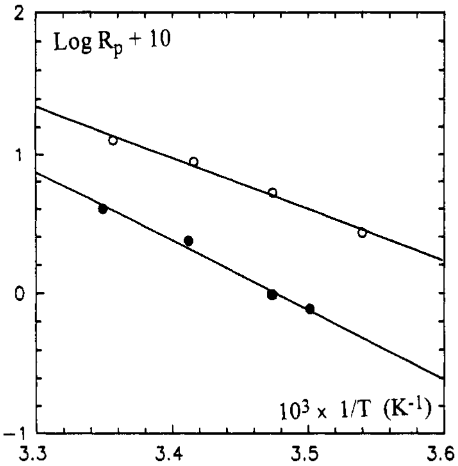
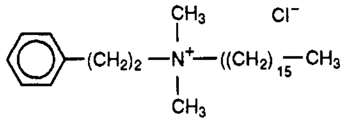


Figure 9. Arrhenius plot for the polymerization rate of C8-STY (○) and C16-STY (●).

pounds is fairly high (≃30–50 kJ/mol) whereas the termination activation energy is often low (≃10 kJ/mol or less),[30] and our results are consistent with these values.

Discussion

Prior to a discussion on the mechanism of micellar polymerization, it is important to determine the main locus for monomer initiation: continuous aqueous phase and/or micelles. We recall that the problem of the locus of initiation in emulsion polymerization has been and is still the topic of much discussion.[31] Such a determination requires first the knowledge of the partition coefficient K_p of the hydrophobic initiator DMPA, between the micelles and continuous aqueous phase (solubility of DMPA in water: 2.5×10^{-4} M). We have used UV absorption for the determination of K_p. As the polymerizable surfactants show an absorption peak at the wavelength used to monitor DMPA (λ = 250 nm), the experiments were carried out on the surfactant hexadecyldimethyl(phenylethyl)ammonium chloride (C16-EC) of the chemical structure



(7)

C16-EC

This surfactant is very closely related to C16-STY and should exhibit similar solubilization properties. UV measurements yielded the value $K_p = 2.3 \times 10^4$ for the partition coefficient of DMPA between C16-EC micelles and water. Simple calculations based on this K_p value indicate that, in the C16-STY concentration range investigated, 84–89% of the initiator is bound to the micelles. This result, in conjunction with the high local concentration of surfactant monomers in the micelles, supports the sound hypothesis that initiation essentially occurs within the micelles, in the case of C16-STY.

The two following polymerization mechanisms can be put forward, depending on the surfactant cmc value.

1. **Case of Low Cmc Surfactants.** The C16-STY compound is a good example of this situation. Its cmc in water is very low (2.9×10^{-4} M). In the C range covered (0.02–0.1 M), this surfactant is thus essentially in the micellar state before polymerization (Figure 10A). It is most probable that initiation starts within a micelle containing one initiator molecule. With the values of [I] and C used, the fraction of such micelles amounts to 0.04–0.18.[22] The propagation mode will depend upon the lifetime T_M of the initial micelles. Recall that

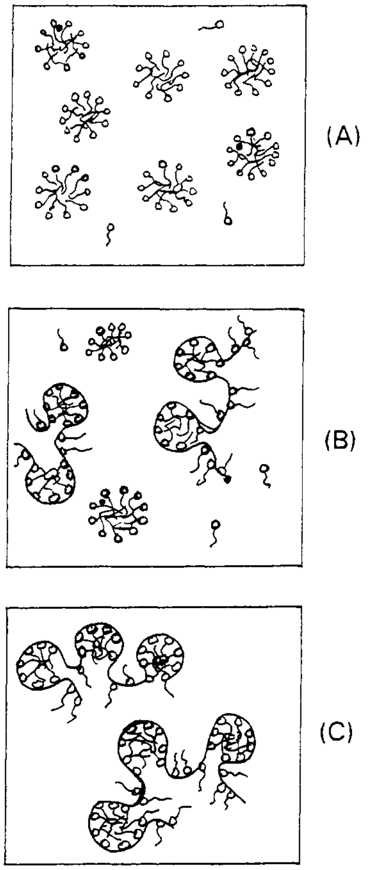


Figure 10. Schematic representation of the micellar polymerization of a surfactant with a low cmc. (A) Before polymerization (● represents an initiator radical). (B) Same solution in the course of polymerization. (C) At the end of the polymerization. The schematic representation of the polymer particles is based on the results reported in part 1.[22]

$$T_M = N\tau_2 a[1 + \sigma^2/Na]^{-1} \qquad (8)$$

where τ_2 is the relaxation time associated with the formation breakdown of the micelles,[32] $a = (C - \text{cmc})/\text{cmc}$, and σ is the standard deviation of the aggregation number distribution. For $C \gg$ cmc (case of C16-STY), $a \gg 1$ and $T_M \simeq N\tau_2$ since it is usually found that σ^2/N is close to 1.[33,34] For a long alkyl chain surfactant such as C16-STY, τ_2 can be much larger than 10^{-3} s,[35] and for $N = 50$,[22] one obtains $T_M \gg 5 \times 10^{-2}$ s.

Thus, the micelle lifetime can be very long. This fact was not taken into much consideration in previous studies[36] of micellar polymerization which essentially focused on the mean residence time, T_R, of a unimer in a micelle. This time, which is on the order of 10^{-4} s for a C16 surfactant,[34,35] is much shorter than T_M. On the basis of the comparison of T_R with the time required for the addition of a styrene monomer to a growing radical (about 10^{-3} s), it was concluded that the micelles are too labile for a significant propagation of the polymerization in a given micelle.[36] We believe that this conclusion is not correct in the case of surfactants with low cmc, where the micelle lifetime is generally long.

Once initiation occurs within a micelle containing a DMPA molecule, this micelle persists in the solution during an average time T_M, although its aggregation number fluctuates rapidly (time scale T_R) around the average value N. Since the time required for the addition of a styrene monomer to a growing radical is about 10^{-3} s,[36] an oligomeric radical containing 20–100 repeat units (that is, all the monomers constituting a micelle) may be formed after a time close to T_M. Such a radical, in turn, will considerably stabilize the micelle owing to its high hydrophobicity relative to that of the monomeric surfactant. The latter argument is supported by the large decrease in cmc observed when replacing a monomeric surfactant by its dimer,[37] and it is known that the cmc provides direct information on the micelle dynamics.[34] Thus, the oligomeric radical will keep growing to give rise to a polymer of high M_w, by being fed monomeric surfactants from unnucleated (empty) micelles (Figure 10B). Notice that the time t_A required for the association of a surfactant monomer to a micelle is very short. It is given by $[k^+ \times \text{cmc}]^{-1}$. With $k^+ \simeq 10^9$ M^{-1} s^{-1} [33] and cmc $\simeq 10^{-4}$ M, one obtains $t_A \simeq 10^{-5}$ s. As required, this time is much shorter than that for the addition of a styrene monomer to a growing radical. Therefore, during the whole polymerization process, the reaction medium contains micelles together with dead or growing polymer particles. The active polymer particles grow at the expense of the noninitiated micelles, since the monomer concentration within the growing particles is below its equilibrium (saturation) level. This induces a net flow of monomer from unnucleated micelles toward active particles until total disappearance of the former (Figure 10C).

This mechanism is, in some way, similar to that of emulsion polymerization[31] and, even more so, of microemulsion polymerization[38] in which a constant monomer feed is set up from unnucleated micelles toward active ones by either diffusion or collision between active and inactive particles. Monomer diffusion should be the dominant process in the aqueous micellar solutions considered here since they are electrostatically stabilized, making collisions very unlikely. Chain termination can occur either by radical capture or by bimolecular reaction between two growing polymer radicals. Concerning the latter point, it was shown in part 1[22] that the polymeric particles do not grow in complete isolation and have thus the possibility of mutual termination.

Another analogy between microemulsion polymerization and polymerization of micelle-forming monomers (with low cmc) is the continuous particle nucleation observed throughout the course of polymerization. For the former process, it was shown that this resulted in a uni-/oligomolecular polymerization where one to few polymer chains are intra- and/or intermolecularly collapsed within small-sized stable latex particles.[38] This mechanism differentiates microemulsion polymerization from other processes in dispersed media. In emulsion polymerization, for example, the particle nucleation only occurs at the early stages of the reaction (interval I).[24] During the remainder of the reaction, the number of particles remains constant and these particles continue to grow due to diffusion of monomer from reservoir droplets through the continuous medium.[31] Thus, at the end of the reaction, these latex particles may contain thousands of polymer chains.

The above mechanism which holds for surfactants containing polymerizable groups of high reactivity excludes the possibility of a topological polymerization i.e., a polymerization in which the polymer corresponds very closely to the original monomer micelle as far as molecular weight and structure are concerned. If the monomer reactivity is low, the polymers formed will have a much smaller degree of polymerization, the termination reactions competing then with the propagation reaction. It should, however, be underlined that, in such a case, the oligomeric radical formed in a micelle after a time T_M is very short and does not prevent the micelle breakdown. This takes the oligomeric radical in the solution where it may (i) react with another growing polymer radical (termination); (ii) grow by reacting with monomer (slow reaction rate due to the low cmc); (iii) associate with an unnucleated micelle in which it could keep on growing; or (iv) act as a germ for the formation of a micelle, because it is more hydrophobic than the monomer. In all these cases, one expects low degrees of polymerization, in agreement with the experimental results observed for the micellar polymerization of sodium 10–undecanoate[9,17,39] or allyldimethyldodecylammonium bromide,[18] and highly polydisperse polymers with even the possibility of a bimodal distribution. Since the micelle aggregation numbers are small, the result of the polymerization reaction may lead to the erroneous conclusion that a topological polymerization of the micelles was achieved.

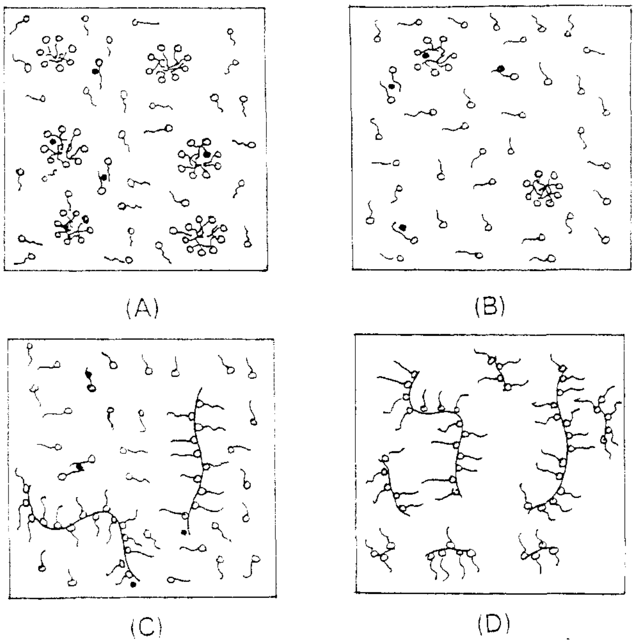


Figure 11. Schematic representation of the micellar polymerization of a surfactant with a high cmc. (A and B) Solutions before polymerization at C = 2cmc and C = 1.2cmc, respectively. (C) Same solutions after time t_1: the uninitiated micelles have been consumed. (D) Solutions at the end of the polymerization.

2. Case of High Cmc Surfactants. This situation is represented by C8-STY (cmc = 0.088 M).[22] In the range of surfactant concentration studied (0.1–0.2 M), the fractions of free and micellized C8-STY are comparable. In contrast to the previous case, an important part of the initiator (likely about 30–50% in the present case) is now solubilized in the intermicellar phase because of the lower value of K_p due to (i) the smaller size of C8-STY micelles with respect to C16-STY micelles and (ii) the high cmc value of C8-STY which significantly increases the water solubility of DMPA. It ensues that homogeneous nucleation can effectively compete with micellar nucleation. Nevertheless, both initiation and polymerization rates must be much larger in the micellar phase, owing to the very high local surfactant concentration.

Consider first the case where the micellized surfactant concentration is close to that of free surfactant, i.e., C = 2cmc (Figure 11A). As for C16-STY, nucleation and growth mainly occur in the micelles (local monomer concentration $\simeq$ 50cmc). However, the growth stage occurs in a more complex manner than in the case of a low cmc surfactant. The lifetime of high cmc micelles is indeed much shorter as τ_2 is now on the order of 10^{-6} s;[35] hence, the T_M values are well below 10^{-3} s. This allows at most the formation in the micelle of a radical IM$^\bullet$ by addition of a monomer M to an initiator radical $I^\bullet$. The radical $IM^\bullet$ is not hydrophobic enough to stabilize the micelle, which breaksdown after a time T_M and $IM^\bullet$ propagates in the aqueous phase or acts as a germ for the formation of a micelle, where the polymerization continues. Repetition of these processes can lead to polymers of high $\bar{M}_w$ only if the reactivity of $IM^\bullet$ is high enough (as seems to be the case for the C8-STY). If not, low $\bar{M}_w$ polymers are obtained (case of monomers with an allyl group). After a time t_1, the system only contains free surfactants together with dead or growing polymer molecules (Figure 11C) and the polymerization continues in the aqueous phase. This mechanism accounts for the slowing down seen in the conversion vs time curves for C8-STY as opposed to C16-STY.

In the case of micellar solutions at C only slightly above cmc (for example, C = 1.2cmc or below cmc) (Figure 11B), the polymerization in the homogeneous phase becomes the predominant or unique process, accounting for the strong decrease of R_p and the departure from linearity observed in Figure 4, when C is close to the cmc. The time t_1 is also reduced. In part 1,[22] it was shown that the polymer particles formed from C8-STY have a typical polyelectrolyte behavior. It follows that the termination reaction should proceed as for free-radical polymerization in homogeneous solution, i.e., by combination or disproportionation of two growing polymer radicals.

The above mechanistic scheme does not take into account possible transfer reactions or radical desorption from the micelles during polymerization. Concerning the first point, the high molecular weights of the polymers formed are in favor of limited transfer reactions. The methylene group located in the α position to the aromatic nucleus contains a labile hydrogen. However, the proximity of the quaternary ammonium ion may inhibit the transfer reaction from the polycation to a monomer because of electrostatic repulsion. In addition, steric hindrance should also prevent such reactions.

Conclusions

We have prepared polymerizable surfactants, the alkyldimethyl(vinylbenzyl)ammonium chlorides referred to as C*n*-STY with n = 8 and 16. These surfactants have been photochemically polymerized in the micellar state using an oil-soluble initiator. The rate of polymerization of C8-STY and C16-STY and the molecular weight M_w of the polymers thus prepared have been found to scale with the monomer concentration C and initiator concentration [I] according to $R_p \propto [I]^\alpha C^\beta$ and $\bar{M}_w \propto [I]^\gamma$ where the exponents α, β, and γ have values close to those characteristic of radically initiated emulsion polymerization. On the basis of the site of solubilization of the initiator (located mostly in the micelles in C16-STY solutions but about equally partitioned between the micelles and bulk phase for C8-STY solutions), we have proposed a mechanism for the micellar polymerization which distinguishes between surfactants having high and low cmc values and strongly emphasizes the importance of the value of the micelle lifetime on the course of the polymerization. Systems with long-lived micelles have small cmc (case of C16-STY) and the polymerization essentially takes place in nucleated micelles, which grow at the expense of unnucleated ones. These micelles become progressively more stable as polymerization proceeds because of the increased hydrophobicity of the polymer formed with respect to the monomeric surfactant. Systems with short-lived micelles have a high cmc, and the micelles break down before a sufficiently long polymer is formed. Polymerization then proceeds both in the aqueous phase and in micelles. The proposed mechanism completely excludes a topological polymerization of the micelles.

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