Macromolecules **1999,** *32,* 2679−2683

Miniemulsion Polymerization with Cationic and Nonionic Surfactants: A Very Efficient Use of Surfactants for Heterophase Polymerization

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Received December 17, 1998

ABSTRACT: The principle of miniemulsion polymerization is extended to cationic surfactants, i.e., CTAB, $CTMA_2$ tartrate, and $CTMA_2$ terephthalate, and nonionic surfactants, i.e., Lutensol AT50. Similar molecular amounts of the cationic surfactant CTAB compared to the anionic surfactant SDS result in similar particle sizes. The cationic counterion-coupled gemini surfactants (cocogems) show only moderate activity in miniemulsification. Surface tension measurements were used to determine the surface coverage and therefore the efficiency of the surfactants in the miniemulsification process. The data for the different latexes show that the underlying energetic rules of miniemulsions are different from microemulsions. It is speculated that for miniemulsions the ability for surface spreading is advantageous whereas low absolute interface energies and a high area requirement per surfactant are favorable for microemulsions. Reaction calorimeter data are also presented to show that the concept of the miniemulsion polymerization is essentially a 1:1 copying of the original droplets, possessing no complicated dependence of kinetics and particle size on the amount and locus of initiation as found for emulsion polymerization.

Introduction

Miniemulsions are dispersions of relatively stable oil droplets, with a size in the range 50−500 nm, in water prepared by shearing a system containing oil, water, surfactant, and cosurfactant (or hydrophobe).[1] Polymerization in such miniemulsions, when carefully prepared, results in latex particles which have about the same size as the initial droplets, as recently shown by a combination of SANS, surface tension measurements, and conductometry.[2] This means that the appropriate formulation of a miniemulsion suppresses coalescence of droplets or Ostwald ripening. To achieve the one-to-one copy of droplets to particles, it is important to create a rather stable starting situation, characterized by small primary droplets with a narrow droplet size distribution, by using high homogenization intensities for a small volume of homogenization.

Up to now, practically all miniemulsion recipes were based upon the anionic surfactant sodium dodecyl sulfate (SDS) in combination with selectively oil-soluble cosurfactants or hydrophobes such as cetyl alcohol, hexadecane, dodecyl mercaptan,[3] or reactive alkyl methacrylates. However, for a number of applications, such as coating of negatively charged surfaces, cationic or nonionic latexes are required, and it is an open question whether the advantages of a miniemulsion polymerization can be transferred to such systems.

The synthesis of cationic latexes by conventional emulsion polymerization is reported in the literature in a few cases, but usually large latexes are obtained and rather large amounts of surfactant are required.[4] It is well-known that cationic latexes can, on one hand, easily be produced in a microemulsion-based process. The majority of microemulsions described in the literature are based on the cationic surfactants dodecyl trimethylammonium bromide (DTAB)[5] or the longer chain surfactant cetyl trimethylammonium bromide (CTAB).[6,7] Recently it was shown that the geometry and the polarity of a given cationic surfactant can profitably be adjusted by electrostatic coupling with organic counterions composed of sterically demanding, functional groups.[8] In this paper, we will employ both standard cationic and organically modified cationic surfactants to synthesize cationic latex particles by miniemulsion polymerization.

For the synthesis of uncharged miniemulsions, polymerizations are performed in the presence of a nonionic stabilizer, a poly(ethylene oxide) derivative. For all systems, the surface tensions of the final latexes as well as surfactant titrations are used to determine the surface coverage of the latexes, and with that the efficiency of the miniemulsification process is characterized. It will be shown that such miniemulsion routes use surfactants in a far more efficient way than microemulsion polymerizations and are as efficient as the best emulsion polymerization recipes.

The influence of the type of surfactant on the size of other latexes as well as the differences in the polymerization rate is discussed. In addition, we will compare the effect of a surface active cationic initiator (where the reaction is started close to the interphase and radical desorption is expected to have a great effect) with that of the nonionic initiator AIBN (where the reaction is initiated in the droplets and a diffusion of radicals through the water phase is less likely).

Experimental Section

The cetyltrimethylammonium (CTMA) surfactants with different counterions are synthesized by exchanging the chloride of CTMA−Cl with the bulky counterions terephthalate or tartrate using an extraction process described in detail elsewhere.[8] The surfactant Lutensol AT50 is a poly(ethylene oxide)−hexadecyl ether with an EO block length of about 50 units.

For preparing the miniemulsions, 6 g of styrene as monomer and 250 mg of hexadecane as hydrophobe were mixed and added to a solution of the surfactant (CTMA−Cl, $CTMA_2$ tartrate, $CTMA_2$ terephthalate, or Lutensol AT50) (for quantities see Table 1) and 24 g of water. After stirring for 1 h, the miniemulsion was prepared by ultrasonifying the emulsion for 60 s at level 5 with an ultrasonic disintegrator, type UD-20, by Techpan. The temperature was then increased to 70 °C, and the polymerization was started by adding 120 mg of V50.

10.1021/ma9819438 CCC: $18.00

Table 1. Characteristics of the Latexes

surfactant	[surfactant] (mM)[a]	*S* (%)	initiator	diam d_I (nm)	std dev	A_{surf} (nm^2)	σ (mN m^{-1})
SDS	10	1.2	KPS	138	0.086	1.66	56.8
	20	2.4	KPS	93	0.150	1.21	60.0
CTAB (CTMA Br)	10	1.5	V50	120	0.223	1.96	66.3
	10	1.5	AIBN	116	0.264	2.02	63.4
	20	3.0	V50	86	0.044	1.14	59.0
	20	3.0	AIBN	89	0.188	1.12	58.7
$CTMA_2$ terephthalate	10	1.5	V50	201	0.518	0.98	53.1
	10	1.5	AIBN	167	0.188	1.14	53.3
	20	3.0	V50	113	0.164	0.91	52.8
	20	3.0	AIBN	137	0.133	0.76	47.4
$CTMA_2$ tartrate	10	1.5	V50	165	0.092	1.25	55.4
	10	1.5	AIBN	120	0.214	1.63	60.7
	20	3.0	V50	90	0.181	1.17	55.6
	20	3.0	AIBN	99	0.259	1.05	54.6
Lutensol (AT50) ($C_{16}/C_{18}EO_{50}$)	3	3.0	AIBN	299	0.423	2.57	56.0
	5	5.0	AIBN	179	0.243	2.58	54.7

[a] Based on the water phase and corrected for the number of tails.

In the case of AIBN as an initiator, 150 mg of AIBN was added to the oil phase prior to ultrasonification, and the reaction temperature was kept at 65 °C. The results were compared with latexes synthesized with the anionic surfactant sodium dodecyl sulfate where the molar ratio of surfactant to monomer was chosen to be the same. The type of surfactant used here does not seem to cause severe chain transfer reactions.

For reactions in the reaction calorimeter, the 3-fold charge as before was used. The time of ultrasonification was extended to 15 min to reach equilibrium. To avoid any polymerization due to heating of the sample, it was ice-cooled during the homogenization.

The calorimetric measurements were carried out in a reaction calorimeter RM2-S from ChemiSens (Lund, Sweden) with a volume of 100 mL equipped with a stainless steel stirrer and a heating facility through the bottom of the reaction vessel.

For the samples with preadded polymer, 360 mg (2 wt %) of an anionically synthesized polystyrene ($M_w = 244\,500$ g mol^{-1}) was dissolved in the monomeric phase.

All measurements regarding the surface tension were performed with the K12 processor−tensiometer from Krüss employing the DuNöuy-Ring method. The radius of the Pt−Ir ring, RI12, was 9.545 mm, and the wire had a radius of 0.185 mm. Each measurement was repeated 10 times, and the obtained values were corrected according to Zuidema and Waters.[9]

Titration of the particle surfaces by measuring the surface tension of the latex was carried out by successively adding 0.2 mL of a 12 g L^{-1} solution of the corresponding surfactant to 40 mL of the latex. Following each addition the latex was stirred for 60 s before the surface tension was determined.

The particle sizes were measured using a Nicomp particle sizer (model 370, PSS Santa Barbara) at a fixed scattering angle of 90°.

The surface charge densities were determined with a particle charge detector (model PCD02, Mütek).

Results

The data of the miniemulsion polymerization reactions with the different surfactants and initiators are summarized in Table 1. The table includes the data on the weight ratio of SDS to monomer, the particle sizes with their standard deviations, the data on particle surface area per SDS molecule A_{surf}, and the surface tension of the latexes.

Latexes were synthesized with the cationic surfactant CTAB at the same molar amount of surfactant as in the case of previously synthesized SDS latexes. With 10 mM CTAB and V50 as initiator, one obtains particles with about the same diameter, 120 nm. The surface area per surfactant molecule as calculated from the stoichiometry, particle size, and the simplistic assumption that all or most surfactant molecules are located at the droplet surface for this system (10 mM CTAB/V50) is 1.96 nm^2 (and therefore well above the value of a dense CTAB surfactant layer), whereas for the latex with 20 mm CTAB, the particles are smaller (86 nm) and the surface area per surfactant decreases to 1.14 nm^2. In general, the data are comparable to those obtained with the anionic reference system, SDS; this means that it is possible to formulate cationic miniemulsions with the same efficiency. It is also noted that the polydispersities are in general rather small; i.e., standard deviations of the distribution functions are usually below 0.2.

The reactions with the cationic gemini surfactants $CTMA_2$ terephthalate and $CTMA_2$ tartrate showed that there is no specific advantage to use such supramolecular gemini surfactants for miniemulsion purposes: About the same results are obtained for the tartrate, while for terephthalate the particles are larger than for simple CTAB. This is also nicely seen in the values of the surface area per surfactant molecule. (Note that the molar amount is related to the tail concentration or to the number of CTMA chains.) This behavior is opposite to the microemulsion process where such surfactants are superior and denotes a clear mechanistic difference between the two techniques. The reason for this difference with respect to surfactant properties will be discussed below.

We also compared the influence of a water-soluble and interface active initiator, V50, with the oil-soluble AIBN at otherwise unchanged polymerization conditions. It is interesting to note that practically no difference was obtained for CTAB, which goes well with the idea that, in the limit of an ideal miniemulsion, polymerization is a 1:1 copying process, where particle size does not depend on the type and amount of initiator.

The situation is more complicated for $CTMA_2$ terephthalate and $CTMA_2$ tartrate, where no clear trend for the role of the initiator becomes visible: the cationic initiator increases the particle size for low surfactant loads, whereas particles become smaller for higher amounts of surfactant. This effect is apparently not due to the polymerization but connected to different particle sizes of the miniemulsion droplets prior to polymerization. It can be shown by surface tension measurements that V50 is highly surface active and can contribute to stabilization of the particles; in addition, due to its ionic character, it can exchange with the surfactant counterions, thereby changing the cocogem. The surface charge density of the V50 initiated latexes stabilized by coco-

Table 2. Results of the Surface Tension Titrations of Different Latexes and the Calculated Surface Coverages

latex	surfactant	diam (nm)	[surfactant] in latex (mmol L^{-1})	kink (mM L^{-1})	cmc of surfactant (mmol L^{-1})	[surfactant] at surface (mol L^{-1})	surface coverage (%)	A_{surf} at full coverage (nm^2)
NBME3	SDS	138	10.4	36.5	8.2	28.8	28	0.48
DOME61	CTAB	116	10.0	33.8	1	32.8	30	0.62
DOME23	$CTMA_2$ tartrate, V50	122	22.5	24.2	1	23.2	93	0.81
KLCM8	$CTMA_2$ terephthalate, AIBN	123	25.2	26.7	1	25.7	94	0.85
KLCM11	$CTMA_2$ tartrate, AIBN	114	24.6	27.2	1	26.2	90	0.86

gems was determined to be 25 μC cm^{-1}, while both systems initiated with AIBN possess a lower surface charge density of 9 μC cm^{-1}. This underlines that V50 significantly contributes to the surface charge structure, which makes a quantitative discussion of the presented data very difficult. On the other hand, this surface charge titration shows that the cocogems are only weakly dissociated, i.e., act as the condensed zwitterions rather than via a dissociated species.

Table 1 also includes data for miniemulsions with small particle size distribution successfully produced using the nonionic oligomeric surfactant Lutensol AT50. Even with a relatively low concentration of surfactant (3−5%), stable latex particles are obtained with particle sizes of 300 and 180 nm. The area per surfactant molecule is about 2.5 nm^2. The apparent lower surfactant efficiency with respect to the weight fraction of surfactant, *S*, is typical for nonionic surfactants and is related to the fact that about the same surface area is stabilized by a far longer nonionic oligomeric chain. It is also noted that the same surfactant was used in the microemulsion polymerization, however with higher surfactant loads.[10]

Surface Tension Measurements. It has already been stated above that, for most described miniemulsions, the surfaces of the particles are not completely covered by surfactant molecules, as indicated by the calculated idealized surface area per molecule. In principle, there is an equilibrium between the surfactant molecules on the particle surface, in the water phase (molecularily dissolved or as micelles), and at the latex/air surface. Fully covered latex particles would allow the surfactant to form micelles in the water phase, and the interface energy toward air would reach the value of a saturated surfactant solution. Higher surface tension, on the other hand, proves that there are no free micelles in solution, or in other words, the surface tension of the latex is a good measure for the coverage of the polymer particles with surfactant molecules. It is shown in Table 2 that most latexes have a surface tension between 47 and 66 mN m^{-1}, i.e., are significantly above that of a saturated surfactant layer. The equilibrium surface tension values for the CTMA surfactants (independent of the counterion) and the Lutensol AT50 are about 35 and 45 mN m^{-1}, respectively. Plotting the surface tension against the calculated A_{surf} values, as performed in Figure 1, it is seen that both properties correlate: the lower the surface coverage of the particles, the higher the surface tension of the latex dispersion toward air.

Titration of the final latex with a concentrated surfactant solution while measuring the surface tension allows quantification of the relative surface coverage with surfactants. Figure 2 shows, as an example, the titration of one of the SDS latexes.

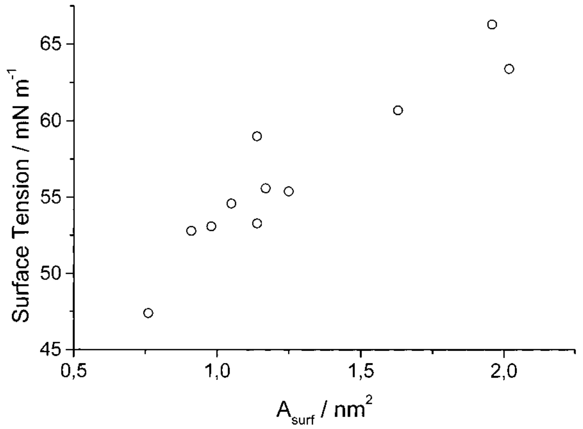

Figure 1. Surface tension versus the calculated A_{surf} values.

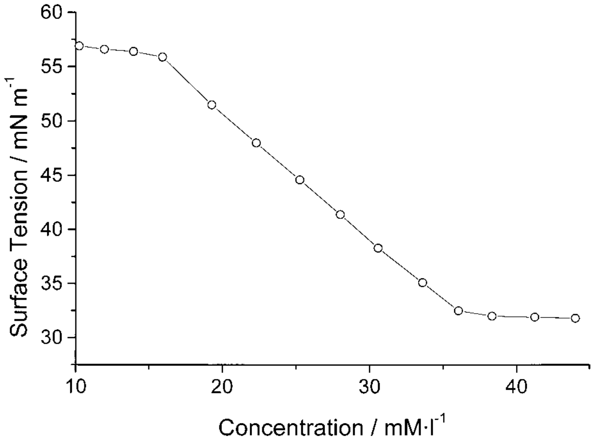

Figure 2. Surface tension titration of the latex synthesized with SDS (*d* = 138 nm, solids content, 18.91%).

The original latex as synthesized showed a surface tension of 56.8 mN m^{-1} and contained 3 g L^{-1} (10.4 mM L^{-1}) surfactant. Recording the surface tension with the addition of surfactant results in a "cmc-like" kink at a surfactant concentration of 36.5 mM L^{-1}. Subtracting the cmc of a pure SDS solution, 8.2 mM L^{-1}, which is taken as a measure for the amount of nonlatex bound surfactant present in the colloidal solution, we easily estimate a full surface coverage at 28.3 mM L^{-1}. Therefore, the original latex had a surface coverage of 36.4%. This goes very well with the A_{surf} value of 1.66 nm^2, as compared to A_{surf} = 0.56 nm^2 of a dense SDS layer.[11]

A number of the other systems have been titrated in a similar fashion; the resulting data are summarized in Table 2.

It is seen that the surface coverage of CTAB is also very low; i.e., for this cationic system the miniemulsion process makes very effective use of the surfactant. This is rather untypical for cationic latexes in emulsion polymerization. The surface coverage of the cocogem latexes is rather high and just slightly below complete surface coverage. A speculative interpretation for this observation is that these supramolecular surfactants prefer close packing due to the counterion coupling, i.e.,

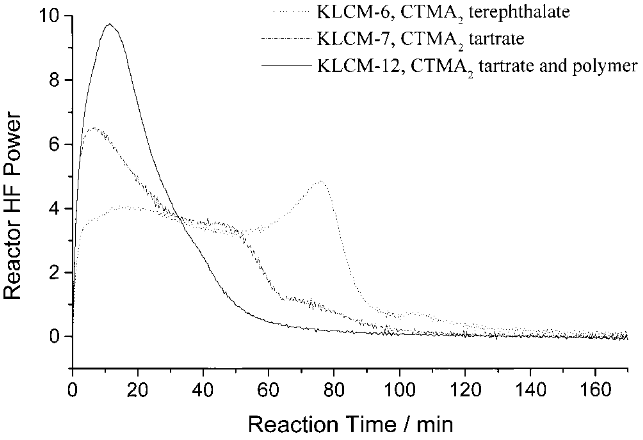

Figure 3. Calorimetric measurements with V50 as initiator.

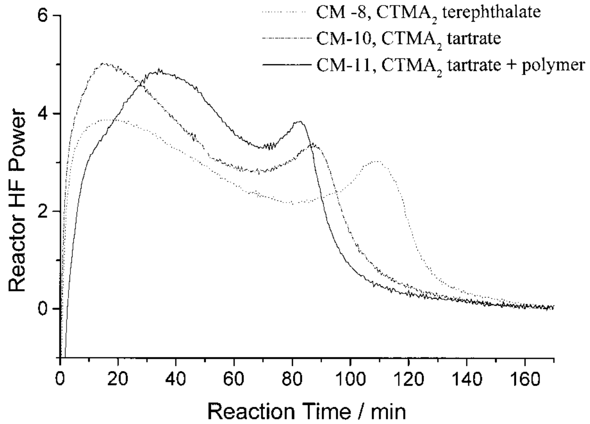

Figure 4. Calorimetric measurements with AIBN as initiator.

the surface extension modulus is quite high, and incomplete coverage is energetically very unfavorable. The higher solubility of the cocogems in the monomer compared to the case of CTAB is of secondary importance, because both the surfactant ion and its counterion will still be very close to the oil/water interface. This interpretation, however, has to be supported by additional experiments.

Kinetics. The kinetics of the miniemulsion polymerization were investigated for the V50 and AIBN initiators and the three different cationic surfactants. The reactions with V50 are shown in Figure 3. Due to differences in the decomposition rate of the anionic and cationic initiators, KPS and V50, data for the anionic system are not presented here.

The reaction with terephthalate shows a rapid increase in the polymerization rate as typically observed for other miniemulsion polymerization processes.[13] After an almost constant regime, the polymerization rate increases toward the end of the reaction, indicating the gel effect. In comparison, the polymerization of the tartrate latex decreases after a first sharp increase, and the gel effect is much less pronounced. For SDS systems, it was reported[12] that an addition of 1% polymer to the monomer mixture leads to a shortening of the overall reaction time by a factor of 2. For the cationic surfactant CTMA$_2$ tartrate, this accelerating effect is also found: the reaction time decreases by a factor of 1.5.

The results for AIBN as the initiator are shown in Figure 4. The same characteristics of the curves (a sharp increase in the polymerization rate in the beginning followed by a slight decrease and a final gel effect) are observed for all three samples. Addition of polymer seems to retard the reaction in the early stages but does not significantly change the overall reaction time.

By comparing the calorimetric results of the reactions with the different surfactants and initiators, we observe no large differences between the reactions and the locus of initiation (oil phase versus interfacial initiation; note that the decomposition rates of AIBN and V50 are slightly different). The overall reaction time essentially depends on the number of particles, or in other words, the smaller the particles, the faster the polymerization. This implicates that the monomer droplets are also the locus of polymerization: each monomer minidroplet acts as a minireactor so that more droplets increase the absolute number of growing chains. In such a mechanism, the origin of the radicals is of no importance, since a steady state is rapidly reached. It has to be noted that an acceleration effect with predissolved polymer cannot be observed in the case of AIBN initiation.

Conclusion

It has been shown that the principle of miniemulsion polymerization can be extended to cationic and nonionic surfactants, resulting in a narrow size distribution of stable cationic and nonionic latex particles.

Similar molecular amounts of the simple cationic surfactants, CTAB, compared to those of the anionic surfactant, SDS, result in similar particle sizes, showing that the particle size is essentially controlled by a limit of the surfactant coverage of the latex particles. From surface tension measurement results, this surface coverage was determined to be of the order of 30%, which proves the very efficient use of surfactants in the miniemulsification process.

Two cationic cocogems which were recently shown to be extremely efficient in the formation of microemulsions resulted in only a moderate activity in miniemulsification: rather large latex particles with a close-to-complete surfactant layer were obtained. This shows that the underlying energetical rules of micro- and miniemulsions are different and that efficiency relies on different surfactant properties. It is speculated that for miniemulsions the ability for surface spreading is advantageous whereas low absolute interface energies and a high area requirement per surfactant are favorable for microemulsions.

Nonionic miniemulsions can be made by using 3−5% of a poly(ethylene oxide) derivative as surfactant, resulting in larger, but also very well-defined, latexes.

Reaction rates determined by calorimetry showed no pronounced dependence on the type of initiator or the surfactant besides particle size; this goes well with the concept that miniemulsion polymerization is essentially a 1:1 copying of the original droplets, possessing no complicated dependence of kinetics and particle size on the amount and locus of initiation as found for emulsion polymerization.

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MA9819438