Polymerization in Microemulsion. 2. Surface Control and Functionalization of Microparticles

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ABSTRACT: Polymerization reactions, when performed in microemulsion, result in latex particles with a well-defined size and surface structure. The droplet size is thermodynamically controlled by the amount and character of the surfactant. Such latices have a narrow particle size distribution and sizes of 10 nm $< R <$ 60 nm. Due to the extremely large inner surface of such dispersions (up to 100 m^2/mL), the functionalization of the particle surface during the polymerization step is of scientific and technical interest. In this paper, some general examples of cosurfactants and surfactant mixtures are discussed. In the first two sets of experiments, mixtures of similarly and oppositely charged surfactants are used to examine the sensitivity of these microemulsions to impurities or dopants in the surfactant layer. Subsequently, a study of the influence of functional monomers and block copolymers on the latex particle size and structure is carried out. In all cases, synergetic stabilization as well as a poisoning of the parent microemulsions can be observed. The results of these synthetic procedures are chemically highly active surfaces which could be used for catalysis, for instance.

I. Introduction

The controlled synthesis of well-defined polystyrene latices with hydrodynamic radii between 10 and 60 nm via polymerization in microemulsion has been described in a previous publication.[1] These microemulsions are very simple to create: styrene is dispersed in water using cetyltrimethylammonium chloride (CTMA) or dodecyltrimethylammonium bromide (DTMA) as surfactants; the subsequent polymerization by means of a lipophilic radical initiator (as AIBN) produces a stable latex in high yield. The concentration of surfactant that forms the interphase between the oil and water phases determines the size of the latex particles within a certain range according to a simple geometric model.[1] It must be emphasized that the formation of microemulsions presented in this paper is not supported by cosurfactants such as aliphatic alcohols; these additives would severely disturb the polymerization reaction in the microdroplets.[2]

This simple geometric model of size control as a function of surfactant concentration is valid only in the limiting case of nonpolar monomers. The use of even slightly polar monomers such as methyl methacrylate (MMA) results in smaller droplets than predicted. When methyl methacrylate is incorporated as a comonomer in the polymerization of styrene, a decrease of the particle size also occurs, as well as a marked improvement in particle dispersity. The methyl methacrylate apparently tends to lie at the surface of the polymerized particles and seems in fact to act as a cosurfactant. This positioning at the surface is most likely due to its polarity relative to the nonpolar styrene monomer. The corresponding data are already presented in refs 1 and 3.

This paper describes efforts to utilize this effect in a 2-fold manner. First, surfactant/surfactant and surfactant/cosurfactant mixtures are examined for further improvements in these microemulsions, the goal being smaller latex particles that are more narrowly dispersed and can be produced with less surfactant. Second, the introduction of functionalized comonomers and cosurfactants and the subsequent utilization of the droplet surface for chemical purposes are explored. Considering the very large specific surface area, which is on the order of 10–100 m^2/mL of microemulsion, this control of surface functionality may result in important technological applications.

It will be shown, however, that the surfactant monolayer does not accept all functional groups. Opportunities to functionalize the surface arise only from "self-surfacting" systems in which polar monomers (such as MMA) are enriched in the interface between the polymerized particles and the water phase and support the stability of the microdroplets. On the other hand, a "poisoning" of the interface by comonomers can also be observed, resulting in a breakdown of the microemulsion as seen by the formation of large particles and the presence of a very broad particle size distribution.

Four sets of experiments were investigated: (1) mixtures of CTMA and DTMA, a model for the combination of similar surfactants; (2) mixtures of CTMA and sodium dodecyl sulfate (SDS), a model for differently charged surfactants; (3) various functionalized comonomers which provide for direct and convenient functionalization; (4) mixtures of block copolymers and cosurfactants which also act functionally as ligands or binding sites.

Finally, all data are compared, and some common factors important for successful surface modification are discussed.

II. Experimental Section

The synthesis of the latex particles and their characterization by static and dynamic light scattering and electron microscopy is described in a previous publication.[1] We follow this procedure exactly; only the surfactant and monomer compositions are different.

III. Results

III.1. Mixtures of Similarly Charged Low Molecular Weight Surfactants. In extending the knowledge of surfactant molecule behavior at the interface of such microemulsions, the examination of simple mixtures of two surfactants can yield significant information. It has already been demonstrated that both CTMA and DTMA produce stable microemulsions over a wide range of surfactant concentrations.[1]

Table I compares the data of the pure systems with those of different CTMA/DTMA mixtures. $r_H \equiv \langle r_h^{-1} \rangle_z^{-1}$ is the inverse z-average of the hydrodynamic radius of the

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Table I
Characterization of the Styrene Microemulsion Latices after Polymerization for Different Mixtures of CTMA and DTMA[a]

sample	S_{CTMA}	S_{DTMA}	r_{H}(latex)/nm	u_2
CTMA/0.5	0.5		25.3	0.06
CD/0.45/0.05	0.45	0.05	26.8	0.04
CD/0.25/0.25	0.25	0.25	90	0.25
DTMA/0.5		0.5	24.7	0.04
CTMA/3.0	3.0		10.9	0.11
CD/1.5/1.5	1.5	1.5	14.3	0.09
DTMA/3.0		3.0	9.6	0.06

[a] r_{H} is the hydrodynamic radius of the latex after polymerization as determined by dynamic light scattering; u_2 is the normalized second cumulant at 90° scattering angle. S is the weight ratio (relative amount) of the surfactant to the monomer.

Table II
Characterization of the Styrene Microemulsion Latices after Polymerization for the Mixtures of the Differently Charged Surfactants CTMA and SDS[a]

sample	S_{CTMA}	S_{SDS}	r_{H}(latex)/nm	$u_2(90°)$
CTMA/0.5	0.5		25.3	0.06
CS/0.5/0.05	0.5	0.05	26.1	0.04
CS/0.5/0.1	0.5	0.1	33.2	0.02
CS/0.5/0.2	0.5	0.2	36.0	0.02
CS/0.5/0.4	0.5	0.4	clumping	
CS/0.5/0.5	0.5	0.5	51.5	0.02
CS/0.4/0.5	0.4	0.5	clumping	
CS/0.2/0.5	0.2	0.5	26.7	0.05
CS/0.1/0.5	0.1	0.5	27.4	0.05
SDS/0.5		0.5	52.8	~0
CS/3.0/0.3	3.0	0.3	13.3	0.05

[a] For a definition of the abbreviations, see Table I.

Table III
Characterization of Latices Made with Functional Monomers and Styrene[a]

monomer	comonomer	r_{H}(meas)/nm	$u_2(90°)$
styrene	10% HEMA	24.0	0.03
styrene	10% DAMA	12.5	0.04
styrene	10% GMA	24.2	0.08
styrene	10% MMA	14.2	0.04
styrene		16.4	0.09
MMA		13.5	0.03

[a] The surfactant is in all cases CTMA. r_{H}(meas) is the experimentally determined hydrodynamic radius of the latices; S equals 1 for all reactions. For a definition of the abbreviations, see the text.

polymerized microemulsion droplets. The normalized second cumulants at a 90° scattering angle are directly related to the polydispersities of the latices. It can be shown[4] that this quantity is approximately proportional to $\langle r\rangle_z/\langle r\rangle_w$ of the particles.

For $S = 0.5$ (S is the weight ratio of surfactant to styrene monomer), stable microemulsions are only formed when one component dominates the other. In these cases, the latices are characterized by the same size and polydispersity as the corresponding latices formed in the pure systems. When the CTMA/DTMA ratio approaches 1:1, the particles become unstable and agglomerate to form particles of greater size and much greater polydispersity.

At higher S ratios, the microemulsion becomes stable again, but the droplet size is larger than predicted by the geometric model.[1] For $S = 3$ and $r_{\mathrm{H}} = 14$ nm, we can estimate that only 60% of all surfactant molecules are included in the interface.

For a different project, we have also examined the combination of DTMA and pyridododecyl chloride. A 2:1 mixture results in an unstable microemulsion, whereas mixtures with small amounts of pyridododecyl chloride behave essentially ideally.

Mixing these similarly charged surfactants is apparently not advantageous; the summarized result is a decreased solubilization limit and a loss of surfactant effectiveness.

III.2. Mixtures of Differently Charged Surfactants. In a second set of experiments, we examine the behavior of mixtures of cationic and anionic surfactants. The experimental system is comprised of CTMA, SDS, and styrene. Table II presents the results of latex characterization for this system.

The introduction of SDS improves the properties of the microparticles over a wide range of compositions. Contrary to initial expectations, the microemulsion not only remains stable, but the particle size also becomes more monodisperse.

The mixtures containing 10–30% SDS (with respect to the amount of CTMA) produce particles with comparably small polydispersities. The parent dispersions, when allowed to rest for 2 days at room temperature, form macroscopic agglomerates. This agglomeration is reversible: by increasing the temperature, a homogeneous dispersion is recovered. A mixture of two different particle sizes behaves in the same way, and we can therefore exclude the formation of colloidal macrocrystals as an explanation for this phenomenon. We have to assume that the agglomeration is merely induced by the zwitterionic adduct of CTMA and SDS.

The particle size increases when the relative amount of SDS approaches that of CTMA; close to the balance point, the mixtures become very viscous and precipitate. This precipitation is also thermoreversible. A homogeneous polymerization is obtained again when the relative amounts of CTMA and SDS balance. The microdroplets of this mixture are relatively large but quite narrowly distributed, a fact which indicates a well-defined (complex) surfactant distribution.

Stable microemulsions with smaller particle sizes and distributions are also obtained in mixtures where SDS dominates CTMA. Even the mixture where only 16% of the total surfactant is CTMA forms a stable microemulsion similar in size to that of a microemulsion which is formed largely of CTMA.

This fact is important because pure SDS/styrene mixtures act peculiarly: microemulsions only exist in a small S range (at $S = 0.5$, a pure styrene phase coexists), and, within this range, comparably large droplets with very small polydispersities are produced.[3] Small amounts of CTMA apparently change this behavior to a regular one in which small particle sizes are obtained.

III.3. Addition of Functionalized Monomers. In these experiments, we modify the styrene/DTMA system ($S = 1$) by incorporating one of three different methacryl esters (10% relative to styrene): hydroxyethyl methacrylate (HEMA), (dimethylamino)ethyl methacrylate (DAMA), and glycidyl methacrylate (GMA) (all purchased from Aldrich). In addition, potassium styrenesulfonate, diethyl-(4-vinylbenzyl)amine, and 2-vinylpyridine are used as comonomers.

The last three substances destabilize the microemulsions; only very large and polydisperse latex particles are obtained.

The methacrylate derivatives, however, result in stable microemulsions which are characterized in Table III. Since HEMA and DAMA are water soluble, it is not evident a priori that the monomers are actually incorporated in the interface; alternatively, a polymerization within the water phase could be discussed. For comparison, Table III relates these results to the data for pure styrene and pure

Table IV
Characteristics of Styrene/Vinylpyridine Block Copolymers Which Are Used for Supporting the Formation of Microemulsions[a]

sample	M_w(total)	comonomer	X_{VP}, wt %	M_w/M_n
BC1	3 000	4-VP	54	1.15
BC2	63 000	2-VP	71	1.04
BC3	108 000	2-VP	83	1.07
BC4	200 000	2-VP	91	1.10

[a] For details of the characterization, see ref 9. M_w is the weight average of the overall molecular weight; X_{VP} denotes the relative vinylpyridine content.

MMA as well as for a mixture of both monomers (styrene: MMA = 9:1).

The very small particle size and quite low polydispersity of the DAMA system give direct evidence that DAMA, like MMA, does indeed act as a cosurfactant. Compared to that of the pure styrene microemulsion, the internal particle surface of the 10% DAMA microemulsion has increased by more than a factor of 2.

The existence of surface-bound amino groups can be proven by isolation of the surfactant-free polymer particles (for the procedure, see ref 1). When cross-linked, these particles cannot be precipitated from methanol, as opposed to the analogous styrene microgels. The determination of the surface charge density will be the subject of forthcoming examinations.

The copolymerization of HEMA and GMA with styrene in microemulsion results in particles which are significantly larger than those of pure styrene. These monomers do not support the minimization of surface energy; moreover, they seem to "consume" some of the surfactant. The size distribution of the HEMA particles is as narrow as that of the styrene/MMA system, whereas particles with GMA have a slightly broader distribution. In these two cases, hydroxyl and epoxyl groups must be incorporated at the particle surface, since these microgels also do not precipitate in methanol. In addition, the surface-bound epoxide rings can be easily opened with acidic dyes. Such a reaction results in deeply colored microgels with at least 1 dye molecule per 100 monomer units.

It is interesting to relate these findings with the results of El-Aasser et al.,[5] who examined the distribution of pentanol (used as a cosurfactant) between the different phases in the system styrene/dodecyl sulfate/pentanol/water. They found that pentanol is distributed among all three phases but enriched in the interface. Similar behavior on the part of the comonomers in the systems discussed here would explain the properties of the latices.

III.4. Mixtures of Cationic Surfactants and Block Copolymers. Another class of cosurfactants which are accepted by the primary surfactant and also provide for surface functionalization is block copolymers. The central idea is that a block copolymer consisting of styrene and a polar monomer mimics a surfactant in that it has a nonpolar hydrophobic end and a polar hydrophilic end.

Since we are interested in very small latex particles with some surface-bound "receptor" groups, we have focused on polystyrene/poly(vinylpyridine) block copolymers. For this investigation, five different block copolymers have been synthesized by anionic polymerization following standard routes.[4,5] The characteristics of these systems are listed in Table IV.

A portion of each sample has been quaternated with either methyl bromide or benzyl bromide as described in ref 8. The degree of quaternation is generally above 60%.

Table V summarizes the data of the microemulsions in which the smallest block copolymer (M_w = 3000), both methyl-quaternated and unquaternated, has been incorporated in the microemulsions.

Table V
Data of Polymerized Microemulsions with Block Copolymers Incorporated in the Interface[a]

sample	S	S^*	block copolymer	r_H-(meas)/nm	$u_2(90°)$	comments
U0.1/0.1	0.1	0.1	BC1	48	0.10	
U0.2/0.1	0.2	0.1	BC1	47	0.10	unquaternated
U0.5/0.1	0.5	0.1	BC1	32	0.18	
Q0.1/0.1	0.1	0.1	BC1	36.5	0.05	
Q0.2/0.1	0.2	0.1	BC1	35.2	0.03	quaternated
Q0.5/0.1	0.5	0.1	BC1	24.0	0.04	
A0.2/0.1	0.2	0.1	BC1	27.1	0.04	
A0.2/0.2	0.2	0.2	BC1	55	0.15	with HBr
A0.2/0.5	0.2	0.5	BC1	35.8	0.07	
A0.2/1.0	0.2	1.0	BC1	36	0.12	
S21	0.5	0.029	BC2	34.0	0.05	quaternated
S22	0.5	0.050	BC2	31.5	0.03	
S31	0.5	0.050	BC3	27.1	0.05	quaternated
S32	0.5	0.100	BC3	26.5	0.05	
S41	0.5	0.092	BC4	35	0.11	quaternated
S42	0.5	0.150	BC4	28.3	0.03	

[a] S and S^* denote the relative amounts of CTMA and block copolymer, respectively.

An effective dispersion only occurs when the block copolymer is supported with at least 10% of a low molecular weight surfactant such as CTMA (with respect to styrene). This amount is approximately equal to the solubilization limit of a pure CTMA/styrene system.[1]

Dispersions with unquaternated blocks consist of very polydisperse particles and monomer droplets, as detected by microscopy. (The data in Table V characterize the dispersion only after the droplets have been filtered.) The particles also tend to "clump". In a strict sence, a microemulsion is not formed. Microemulsions possessing quaternated block copolymers, on the other hand, are very well-defined and consist of narrowly distributed particles. The droplet size is much too small to have resulted from the action of the low molecular weight surfactant alone. The quaternated block copolymer clearly acts as a cosurfactant and stabilizes the oil/water interface. In addition, the measured polydispersities are smaller than those of the particles made with CTMA only.

The resulting microemulsion particles possess long poly(vinyl pyridinium) chains protruding from their surface; these chains are "anchored" by means of the styrene blocks which sit inside the polystyrene cores.

Since we are interested in recovering the bare pyridine functionalities after the polymerization step, the original unquaternated block copolymers have also been charged by acidifying the microemulsion during synthesis with a molar equivalent of hydrobromic acid. The characterization of these experiments is also included in Table V.

The procedure succeeds in forming a stable mixed-surfactant surface of CTMA molecules and protonated block copolymers. The microemulsions which possess quaternated and protonated block copolymers are indistinguishable with respect to particle size and polydispersity.

Using the HBr method, various amounts of block copolymer were incorporated in an examination of the extent to which functionalization of the surface is possible through this technique. Holding the CTMA/styrene weight ratio constant at S = 0.2, block copolymer to styrene weight ratios from S^* = 0.1 to 1.0 were examined.

The phase behavior of such a quaternary system is apparently very complex. Increasing S^* from 0.1 to 0.2 destabilizes the microemulsion. This destabilization seems to be similar to destabilization in the CTMA/DTMA system, where identical weight ratios also resulted in an unstable microemulsion. Increasing the block copolymer level to 0.5 again gives a stable microemulsion, demonstrating that surfaces in which either CTMA or the block copolymer dominates are more favorable.

From stoichiometry and particle size one can calculate an effective surface area per block copolymer surfactant. For $S^* = 0.1$, about 600 Å^2 of surface per block copolymer results, whereas the $S^* = 0.5$ microemulsion has only 190 Å^2 per block copolymer. (For comparison, a densely packed CTMA surface has 18 Å^2 per surfactant.) By comparing the square root of the second area (≈14 Å) with the contour length of the pyridinium component of the block copolymer (≈25 Å), we conclude that these molecules do not overlap at the surface.

The $S^* = 0.5$ microemulsion is of course more desirable from a standpoint of functionality, although the presence of too many functional chains may in fact inhibit their effectiveness.

At $S^* = 1.0$, the microemulsion becomes unstable again. From the area calculation, it is logical to attribute this behavior to polymer–polymer repulsion.

In a final set of experiments, the incorporation of larger polyelectrolyte blocks in the interface has also been tested. These cosurfactants were chosen for their potential ability to keep the particles separate through electrostatic repulsion, preventing undesirable clumping within the microemulsion. The particles produced by these experiments can be regarded as polyelectrolyte stars with a nonpolar microgel core in which the number of arms is controlled by S^*. Benzyl-quaternated block copolymers were used in these experiments.

The results are also listed in Table V. We observe that pendant polyelectrolyte chains which are 500 and 1000 monomer units long are well accepted: the resulting microemulsions have low polydispersities and reasonably small sizes. Also in case of the block copolymer cosurfactants, the particle size of the microdroplets does not change during polymerization, as seen by the turbidity of the dispersions (in this context, see also ref 1). Therefore we can exclude coagulative nucleation, and polymerization indeed takes place within the microemulsion droplets.

It must be considered that the experimentally determined radii consist of contributions from the oil core and from a shell of dangling chains. For a separation of these two contributions, static light scattering experiments were also performed for the samples S22, S32, and S42. The molecular weights are 22.7×10^6 (S22), 17.4×10^6 (S32), and 20.4×10^6 (S42). Since the major amount of mass is located in the unswollen latex core, we can calculate a core radius of 18–20 nm from these data. The difference between this core radius and the hydrodynamic radius of the latex (ca. 10 nm) can be attributed to the polyelectrolyte chains.

This value is reasonable, since we expect surface-bound chains to assume a slightly extended conformation, as seen in chains grafted onto a surface[9] and in block copolymer micelles.[10,11]

IV. Comparison of the Data and Discussion

Some consistencies among the four sets of experiments are obvious. Destabilization of the microemulsions is always observed when the amounts of the mixed surfactants are equal. Surprisingly, this is valid even for mixtures of very similar surfactants such as CTMA and DTMA.

Pronounced improvements in CTMA microemulsions with respect to particle polydispersity are observed when small amounts of the oppositely charged SDS surfactants are included. Improvement also occurs in the opposite case: CTMA stabilizes SDS microemulsions. This fact is of practical importance since pure SDS microemulsions possess very large droplets and deviate in their behavior from all other systems. The latices are also improved when minor amounts of MMA, functionalized methacrylate derivatives, and—in some cases—charged block copolymers are used. A lower polydispersity or even smaller micelles are observed.

The common factor in all these systems is that a small perturbation of the surface order of the pure systems is apparently advantageous. The lower polydispersities can speculatively be attributed to an increased fluidity of the interface layer, allowing a better approach to equilibrium and faster exchange among the micelles. The domination of one surfactant ensures coherent stabilization of the droplet whereas a balanced system of two surfactants is too fluid: the microdroplets become unstable.

Smaller particles with low polydispersities are only formed when the cosubstrate effectively disrupts the interface and enables droplet stabilization with a loosely packed surfactant layer. This is valid for MMA, HEMA, and (with some restrictions) the pyridinium block copolymers.

On the other hand, the introduction of amines or unquaternated PVP blocks results in a poisoning of the surface and microemulsion destabilization, probably due to incompatibilities between the dominant structure-forming surfactant and the cosubstrate. Synergistic support through an increase in surface fluidity and surface poisoning are most likely conditions which lie very close to one another. The formation of new microemulsion mixtures is consequently difficult to predict.

V. Conclusion

Polymerization in microemulsion can be successfully used for the direct and convenient surface functionalization of very small latex particles with radii between 10 and 60 nm. For this purpose, two different techniques are applied: (1) copolymerization with functionalized comonomers; (2) introduction of block copolymers as cosurfactants.

Since the stability of microemulsions is very sensitive to impurities or dopants in the surfactant layer, the behavior of a mixed interface is generally complex.

Only two rather flexible rules for successful "surface management" can be derived: (1) In surfactant mixtures, one component must dominate. This component most likely acts as the framework of the droplet interface. (2) The introduction of small amounts of a different active surface component (the nature of which must suit the primary surfactant) improves the quality of microemulsions, as seen by particle size and polydispersity. We can speculate that such behavior occurs through an increased interface flexibility and increased surfactant dynamics due to defects in the interface structure.

The results of particle surface control and particle functionalization are polymer materials which are potentially useful in a variety of applications. For instance, a promising application makes use of the very large inner surface of such a dispersion (10–100 m^2/mL) for the purpose of receptive binding and/or catalysis.

In the use of these products as new materials, the polyelectrolyte stars with microgel cores are also of special interest. The size and number of arms of these structures can be easily controlled via the S and S^* ratios. A more detailed examination of the physical behavior of these systems is presently in progress.[12]

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