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Miniemulsion Polymerization: Applications and New Materials

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SUMMARY: Stable miniemulsions were prepared with cationic (CTAB and $CTMA_2$-tartrate) and nonionic surfactants (Lutensol AT50 and SE3030). The dependence of the latex particle sizes on the amount of the different surfactants showed that ionic surfactants can be more efficiently employed for the synthesis of small particles than the nonionics. For encapsulation of pigments the chemical parameters of the miniemulsion, such as amount and type of the surfactant, have to be chosen so that the final size of the latex corresponds with the size of the pigments. The pigments themselves require a hydrophobic surface in order to enable their embedding into the monomer phase. The successful incorporation of the pigments into the latexes was verified by transmission electron microscopy, freeze-fracture electron microscopy, and the analytical ultracentrifuge.

Introduction

The principle of miniemulsion polymerization for the synthesis of latex particles in the size range between 50 and 500 nm$^{1)}$ extends the possibilities of the widely applied emulsion polymerization with regard to the incorporation of hydrophobic materials$^{2)}$. It was shown earlier$^{3)}$ that miniemulsions are critically stable systems, which can be polymerized directly after the miniemulsification in a 1:1 copying process under retention of the critically stabilized state. A poststabilization with an adequate amount of surfactant allows one to create a stable state where the osmotic pressure and the Laplace pressure is balanced. Reaction rates determined by calorimetry$^{4)}$ showed no pronounced dependence on the type of the surfactant aside from particle size; enhancing thereby the concept of a miniemulsion polymerization essentially being a 1:1 copying process of the original droplets$^{5)}$.

In this paper the efficiency of cationic and nonionic surfactants and the effect of the variation of the amount of surfactant will be discussed. The miniemulsion process is then applied to the encapsulation of different water-insoluble materials such as $CaCO_3$ and carbon black. For a successful encapsulation of hydrophobized $CaCO_3$ into the latex, the importance of the choice of the surfactant is discussed. For encapsulation of carbon black, the role of specifically chosen hydrophobes for the resulting carbon dispersion is shown. The particles

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were characterized in detail by using ultracentrifugation and transmission electron microscopy.

Experimentals

For the synthesis of the latexes, an oil phase of 6 g styrene and 250 mg hexadecane was mixed with 24 g of the surfactant solution containing the aliquot of surfactant as listed in Tab. 1. As cationic surfactants cetyltrimethyl ammonium bromide (CTAB) and the cocogem surfactant cetyltrimethyl ammonium tartrate ($CTMA_2$-tartrate) were chosen[6)]. The nonionic surfactants were Lutensol AT50 which is a polyethyleneoxide-hexadecylether with a EO block length of about 50 units (BASF AG) and the block copolymer SE3030 (30 units of polystyrene, 30 units of polyethylenoxide) (Goldschmidt AG). The mixtures were stirred for 1 hour, and the miniemulsions were prepared by ultrasonifying the emulsions for 60 s at level 5 with a ultrasonic disintegrator type UD-20 by Techpan. The polymerization was started with 100 mg V50 (cationic systems) or 120 mg KPS (nonionic systems) at a temperature of 70 °C. The reaction is usually completed in less than 2 h, as determined by calorimetry[4)].

All latexes were characterized by dynamic light scattering and tensiometry. Experimental details of these techniques can be found elsewhere[4)]. Information about the latexes containing pigments was obtained by dynamic light scattering, the analytical ultracentrifuge and electron microscopy. The density gradient measurements as introduced for encapsulated TiO_2 particles by El-Aasser *et al*[7)]. were obtained by layering different sucrose solutions with densities ranging between 1.0 to 1.3 $g \cdot l^{-1}$ and centrifugating them at 4°C for 120 min at 37,000 rpm in a Beckmann XL-70 ultracentrifuge.

Electron microscopy was performed with a Zeiss 912 Omega electron micrograph operating at 100 kV. For the freeze fracture microscopy, the latex was rapidly frozen at –120 °C in propane cooled in liquid nitrogen and edged for 60 s.

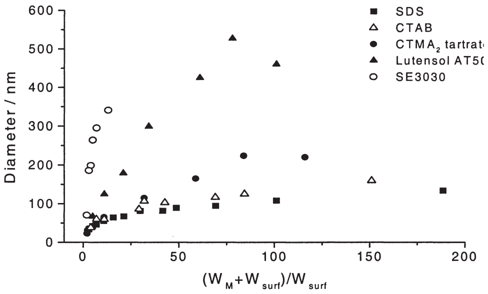

Figure 1: *Dependence of the particle size on the amount and nature of the surfactant.*

Results

The use of cationic and nonionic surfactants

As already reported in an earlier paper[4)] it is possible to obtain stable miniemulsions with cationic surfactants such as CTAB and $CTMA_2$-tartrate and nonionic surfactants such as Lutensol

AT50 and SE3030, respectively. In this paper, the amount of the surfactants was systematically varied over a wide range in order to control the particle size. The data of the miniemulsion polymerization reactions with the different amounts of the various surfactants are summarized in Tab. 1. As seen in Fig. 1, depending on the type of the surfactant different size ranges can be achieved. The particles synthesized with sodium dodecyl sulfate (SDS) or CTAB are very similar to each other, i.e. the efficiency of the surfactant is very similar. By switching the counter ion of the cationic surfactant from bromide to tartrate which turned out to be very effective for microemulsions, the particles become larger indicating its moderate activity in miniemulsification. It was speculated that for miniemulsions a low surface extension modulus of the surfactant layer is advantageous whereas low absolute interfacial energies and a high area requirement per surfactant are favorable for microemulsions. The figure also depicts the obviously lower efficiency regarding the nonionic surfactants in contrast to the ionic ones since a far higher weight fraction of surfactant, S, is needed to obtain particles with a size of about 200 nm. The standard distribution for the particle size are generally broader for the systems containing nonionic surfactants than for those with the cationic surfactants. The surface tension γ can be used as a measure for the coverage of particles$^{4)}$. As can be derived from the surface tension values in Tab.1, the particle surfaces of the latexes are just incompletely covered by surfactant molecules because the surface tensions for the latexes lie between 35 and 66 mN m^{-1}, and therefore well above the values of the saturated surfactant solution. The smaller the particles

Table 1: *Characteristics of the latexes with different surfactants.*

Surfactant	**S [%]**	**Diameter [nm]**	**Standard deviation**	**γ [mN m^{-1}]**
CTAB (CTMA Br)	0.4	347	0.077	58.3
	0.7	159	0.136	60.9
	1.2	125	0.129	61.9
	2.4	102	0.121	61.6
	3.6	86	0.044	60.6
	10.0	59	0.236	49.0
	16.7	59	0.290	43.4
	33.4	38	0.406	35.5
$CTMA_2$ tartrate	0.8	234	0.160	54.7
	1.2	223	0.195	54.9
	3.3	121	0.071	48.7
	20.0	44	0.286	38.2
	50.0	35	0.306	36.1
SE3030	8.3	341	0.213	47.7
	16.6	295	0.488	42.0
	25.0	264	0.374	54.0
	33.3	199	0.264	53.8
	50.0	186	0.260	53.0
Lutensol AT50 ($C_{16}(EO)_{50}$)	1.0	460	0.639	59.2
	3.0	299	0.423	55.9
	5.0	179	0.243	54.7
	10.0	125	0.591	53.0
	25.0	67	0.370	50.2

are, the lower the surface tension is, and therefore, the coverage of the particles with surfactant increases with decreasing particle size. For the CTAB latexes, it is notable that the surface tension remains constant at about 60 mN m^{-1} over a wide range of surfactant concentration. This is in contrast to the other systems where the surface tension depends more on the amount of surfactant used for the latex synthesis. In the case of the polymeric surfactant SE3030, the surface tension changes indifferently indicating that the arrangement of the surfactant due to its polymeric character is more complicated.

Encapsulation of pigments

El-Aasser and coworkers performed pioneer work in the field of encapsulating TiO_2 particles by using miniemulsion polymerization after dispersing TiO_2 pigment particle hydrophobized by OLOA370 in the styrene phase[7]. In order to achieve the incorporation of a pigment into the latex, it is necessary to find the adequate type and amount of surfactant to yield latex particles which have the appropriate size and charge to allow encapsulation. For the preparation of the miniemulsions, two main steps have to be controlled: In a first step, the already hydrophobic or hydrophobized material which is to be incorporated has to be dispersed in the monomer phase. Then, the miniemulsification in the water phase has to be carried out. The hydrophilic pigments themselves require a hydrophobic surface so that they can be dispersed into the hydrophobic monomer phase. In the case of $CaCO_3$, the inorganic nanoparticles were coated with a layer of stearic acid prior to dispersing the pigments into the oil phase. 5 wt% of $CaCO_3$ based on monomer could be successfully dispersed into polystyrene particles. The characteristics of the latexes are listed in Tab. 2.

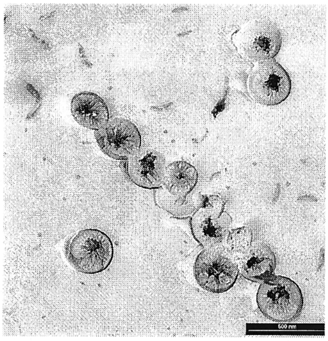

Figure 2: Freeze fraction of $CaCO_3$ particles in styrene shells.

Table 2: *Characteristics of the latexes with $CaCO_3$.*

Latex*	Surfactant	S [%]	Initiator	Hydrophobe wt [%]		Diameter d_I [nm]	Standard deviation
Latexes with $CaCO_3$ (5 wt %), Pigment size: 120 nm							
NBCaME3	SDS	1.2	KPS	HD	4.2	306.9	0.212
NBCaME4	$CTMA_2$ terephthalate	3.4	V50	HD	4.2	149.2	0.178

*All latexes had a solid content of 20 %, HD: hexadecane.

The incorporated pigment could not be directly detected via transmission electron microscopy since the polymer particles were too thick to be penetrated by the electron beam, but it is possible to exclude the presence of free, non-polymer-bound pigment particles. In the latexes synthesized with SDS or CTMA$_2$ terephthalate (amount as indicated in Tab. 2), no free results in formation of a much thinner and therefore electron translucent polymer film which allows visualization of the regular distribution of pigment particles (not shown here). For a further and direct verification we also applied the freeze-fracture technique in order to look inside the miniemulsion droplets. The resulting electron micrographs clearly revealed a rough particulate structure inside most of the particles indicating the effective incorporation of CaCO$_3$ (Fig. 2). The comparison between this sample and an equivalent PS latex without pigment confirmed this interpretation, since the rough structures in the middle of the control latex were not observed.

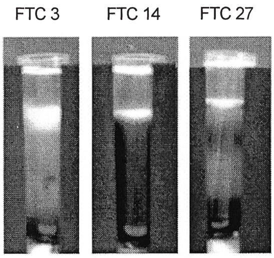

Figure 3: Latexes in the density gradient after ultracentrifugation.

For the encapsulation of carbon black, the type of the hydrophobe is essential to provide full encapsulation of non-agglomerated carbon particles. In this case the hydrophobe not only acts as the osmotic swelling agent for the miniemulsification process to suppress Ostwald ripening, but also partially adsorbs onto the carbon pigment to prevent the formation of rigid aggregates. It was possible to disperse 8 wt% of carbon black in styrene minidroplets. The following hydrophobes could be effectively used for both purposes: hexadecane, Jeffamine M2070 and Jeffamine M1000. The use of the comonomer 9-vinyl carbazole was also successful. The characteristics of the latexes are summarized in Tab. 3. The particles were characterized in detail by using the analytical ultracentrifuge as previously designed for encapsulated TiO$_2$ particles by El-Aasser et al. $^{7)}$ and transmission electron microscopy methods.

The characterization of latexes by ultracentrifugation (UZ) within a density gradient [7] elucidates the distribution of pigments in particles. As seen in Fig. 3, the hybrid particles do show different densities, although in all cases, pure carbon particles could not be found. There are however unfilled, homogeneous PS particles, the amount of which decreases from FTC3 to FT14 and FTC27. In FTC3, a latex synthesized with the comonomer 9-vinyl carbazole and SDS as the surfactant, the carbon containing particles have about the same density whereas in the case of FT14 (synthesized with Lutensol AT50 as surfactant but with the same comonomer), the carbon pigments are inhomogeneously distributed in the PS particles, as indicated by the wide distribution in the density gradient. Latex FTC27 with Jeffamine as the hydrophobe shows two distinct distributions of particle densities.

Table 3: Variation of the hydrophobe and surfactant. The amounts of 3 g styrene, 0.24 g carbon black (8 wt%) and 12 g water were kept constant. The polymerization was started with 70 mg AIBN and the reaction temperature was kept at 68 °C.

Latex	**Surfactant**	**S [%]**	**Hydrophobe wt [%]**		**Diameter d_I [nm]**	**Standard deviation**
FTC 1	SDS	6.6	hexadecane	50	148.6	0.629
FTC 20	SDS	1	polyester [1]	6.6	100.7	0.385
FTC 3	SDS	6.6	9-vinyl carbazole	3.3	123.2	0.724
FTC 25	SDS	1	Jeffamine M2070 [2]	6.6	113.2	0.438
FTC 27	SDS	1	Jeffamine M1000 [3]	6.6	145.7	0.450
FTC 14	Lutensol AT 50	6.6	9-vinyl carbazole	6.6	145.1	0.340

[1] $M_w = 1.33\cdot10^4$ g mol^{-1} synthesized from adipinic acid and 1,6 hexandiol.

[2],[3] The monoamines M1000 and M2070 were constituted of PPO/PEO in a molar ratio of 3/19 and 10/32, respectively with molar weights of 1,000 and 2,000 g·mol^{-1}.

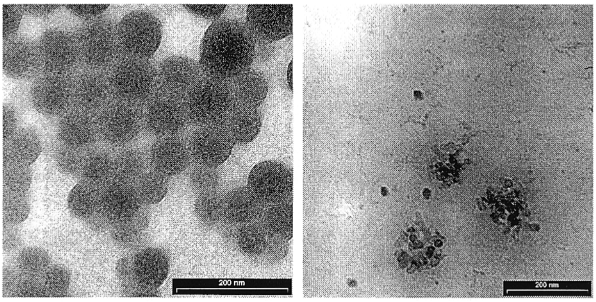

Figure 4: Transmission electron micrographs of a) the original latex and b) the latex annealed at 120 °C.

Transmission electron microscopy of the latex shows spherical and regular particles (Fig. 4a). The incorporated carbon could not be detected via freeze-fracture EM, as in the case of the $CaCO_3$. For all samples, free pigment was not observed. Then the TEM grid with the particles was annealed at a 120 °C over night to result in the thinned polymer film which allows visualization of the pigment particles. Examination of this film revealed partly agglomerated carbon particles (Fig. 4b), as it is quite common for this type of soot, and explains some of the problems of this specific dispersion.

Conclusion

It was shown that the principles of miniemulsion polymerization can be transferred from anionic to cationic and nonionic surfactants. Cationic and nonionic miniemulsions were successfully prepared and polymerized with varying amounts of surfactants in order to realize different size ranges: ionic surfactant can be employed more efficiently for the synthesis of small particles, whereas nonionic surfactants are better suited for the synthesis and stabilization of larger particles.

It was shown that the miniemulsion can be applied to the encapsulation of different water-insoluble materials such as $CaCO_3$ and carbon black. $CaCO_3$ requires a hydrophobic surface that it can be dispersed into the monomer phase. For the encapsulation of carbon, the type of the hydrophobe was found to be essential to provide full encapsulation of weakly agglomerated carbon particles. This points towards the possibilities for further improvement by optimizing the interplay of tailor-made hydrophobes and the carbon in order to minimize the agglomeration of the carbon.

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