Preparation of Polymer Particles in Nonaqueous Direct and Inverse Miniemulsions

Katharina Landfester,* Mirjam Willert, and Markus Antonietti

Max Planck Institute of Colloids and Interfaces, Am Mühlenberg, 14424 Potsdam, Germany

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ABSTRACT: Polymerizable miniemulsions were formulated in nonaqueous media, and it is shown that these systems exhibit characteristics similar to those of aqueous miniemulsions. Depending on the polarity of the continuous medium and the dispersed phase, the formulation of direct and inverse miniemulsions is possible. Direct miniemulsions in nonaqueous media are exemplified by dispersing styrene in formamide or glycol. Inverse miniemulsions were generated with the polar monomer hydroxyethyl methacrylate, acrylamide, or acrylic acid in cyclohexane or hexadecane as the unpolar continuous phase, and the miniemulsions were polymerized to latexes. For both the direct and inverse miniemulsions, it was shown that during high shear dispersion a steady state of droplet size is reached and that addition of a strong lipophobe (for inverse systems) or ultrahydrophobe (for regular systems) is required to stabilize the resulting miniemulsion for sufficient times. With surface tension measurements, the coverage of the particles with surfactant was determined to be incomplete. These facts are typical for the miniemulsion state; i.e., it is proven that organic miniemulsions indeed can be made and polymerized.

Introduction

Regular miniemulsions have been studied for years[1] and can be defined as aqueous dispersions of surfactant stabilized oil droplets within a size range 50−500 nm prepared by shearing a system containing oil, water, a surfactant, and a strong hydrophobe.[2] It was shown that the hydrophobe acts as an osmotic agent which stabilizes the system against Ostwald ripening. The growth of the droplets by collision is controlled by the density of the surfactant layer: freshly prepared miniemulsions are “critically stabilized”[2] and show a slow, but pronounced, growth whereas a miniemulsion in equilibrium exhibit constant particle size on longer time scales.

Polymerization of the oil droplets of such miniemulsions turned out to be very promising and extends the possibilities of classical emulsion polymerization.[3] Due to the fact that the polymerization time is usually shorter than the growth of the droplets by collisions, the polymerization in carefully prepared miniemulsions results in latex particles which have about the same size as the initial droplets, as shown by a combination of SANS, surface tension measurements, and conductometry.[4] In the case of appropriately formulated miniemulsions where polymerization is initiated in each droplet and the solubility of the monomer in the continuous phase is low, the ideal, limiting case of a 1:1 copy of the droplets to the particles can be obtained.

For the formulation of miniemulsions, a wide variation of anionic, cationic, and nonionic surfactants could be used in order to get stable polymer dispersions in different size ranges.[5] Up to now, polymerization reactions in miniemulsion processes are exclusively based on water as the dispersion media.[6,7] For other heterophase polymerization processes the use of other, organic, but polar, dispersion media is reported.[8] Inverse polymerization processes (water-in-oil systems, w/o) employing microemulsions,[9,10] emulsions,[11,12] dispersions,[13,14] and suspensions[15−17] are well-known. The scope of the present paper is to fill this gap and to transfer the principles of miniemulsion polymerization to nonaqueous systems by formulation of polymerizable inverse miniemulsions with the same characteristics as defined above; i.e., we want to produce hydrophilic polymer latexes, ideally by a 1:1 polymerization of the respective monomer minidroplets.

A second, related task is miniemulsion polymerizations of unpolar monomers in the absence of water. Such a procedure is needed when latexes are to be made from water-sensitive monomers (e.g., epoxides, acid chlorides), or a polymerization temperature exceeding 100 °C has to be chosen. Here, the monomers are miniemulsified in highly polar, organic media, and the system again is a dispersion of an organic monomer in an immiscible organic fluid. This case has to be differentiated, since the more polar fluid is the continuous phase, and the dispersion is regular and not inverse.

Experimental Section

Particle Synthesis. (a) Polar Media. A 6 g sample of styrene and 250 mg of hexadecane were mixed and added to a solution of sodium dodecyl sulfate (SDS) or Lutensol AT50 in 24 g of formamide or 48 g of glycol. After 1 h of stirring, the miniemulsion was prepared by ultrasonicating the emulsion for a distinct time, e.g., 120 s, with a Branson sonifier W450 at 90% intensity. For polymerization, the temperature was increased to 72 °C, and 120 mg of potassium persulfate (KPS) was added. In the case of AIBN as an initiator, 150 mg of AIBN was added to the oil phase prior to ultrasonication, and the reaction temperature was kept at 72 °C. If glycol was used, the polymerization was initiated by 120 mg of PEGA200, a poly(ethylene oxide) azo initiator (poly(ethylene glycol)isobutyrate with an ethylene oxide molecular weight of 200 g·mol^{-1}), which was added to the reaction mixture after increasing the temperature. The reaction is usually completed after 2 h.

(b) Nonpolar Media. The monomer and water were mixed and added to a solution of emulsifier in 24 g of the continuous phase (cyclohexane or hexadecane). After 1 h of stirring, the miniemulsion was prepared by ultrasonicating the emulsion for 90 s with a Branson sonifier W450 at 90%. For polymerization, the temperature was increased to 65 °C, and 80 mg of AIBN was added, and the reaction temperature was kept at 65 °C. The reaction is usually completed very quickly after several minutes. To ensure full conversion of the monomer, the reaction mixture was stirred at 65 °C for 2 h.

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Table 1. Surfactants Used for Direct and Inverse Miniemulsions in Nonaqueous Media

Surfactants for Direct Miniemulsions	
SDS	$CH_3(CH_2)_{11}OSO_3Na$
Lutensol AT50	$(C_{16}H_{33})(EO)_{50}$
Surfactants for Inverse Miniemulsions	
Span 80	sorbitane monooleate
KLE3729	poly(ethylene-*co*-butylene)-*b*-poly(ethylene oxide) $M_w = 6600$ g mol^{-1}, 44 wt % EO

The different surfactants used in the direct and inverse case are listed in Table 1. SDS and Span 80 were supplied by Aldrich Co.; Lutensol AT50 is a commercial product of BASF AG, whereas the KLE3729 was kindly supplied by Goldschmidt AG/Essen.

Analytical Methods. Measurements of surface tension or interfacial 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 with the Zuidema and Waters correction.[18]

The particle sizes were measured using a Nicomp particle sizer (model 370, PSS Santa Barbara, CA) at a fixed scattering angle of 90°. The turbidity measurements were carried out by a Process Turbiditymeter (FSC 402, Mettler Toledo, Urdorf, Switzerland) with a sensor for high turbidity values which is sensitive to the backscattered light. This sensor was placed directly into 300 mL of a miniemulsion in a 500 mL beaker in order to avoid backscattering from the glass walls. The wavelength of the light was 880 nm.

For the partitioning experiments of acrylic acid in a two-phase system consisting of water and cyclohexane (ratio 1:10), the components were mixed at 65 °C, and then phase separation was allowed for 1 h. The organic phase was diluted with $CDCl_3$ and analyzed in a Bruker spectrometer at a ^1H frequency of 400 MHz.

Electron microscopy was performed with a Zeiss 912 Omega electron microscope operating at 100 kV. The diluted colloidal solutions were applied to a 400-mesh carbon-coated copper grid and left to dry; no further contrasting was applied.

Results and Discussion

First, tests must be made to see if the characteristic features of miniemulsions can be transferred to nonaqueous systems. The two cases of regular and inverse dispersions rely on different surfactants and have to be differentiated.

In principle, the main characteristics of miniemulsions are the following:

(1) The droplet size throughout the minemulsification process runs into an equilibrium state (steady-state miniemulsion) which is characterized by a dynamic rate equilibrium between fusion and fission of the droplets. The equilibrium can be determined by turbidity measurements.

(2) A partial stability of the droplets after the high shear treatment is obtained by using an osmotic agent which cannot interdiffuse between the single droplets; this creates an osmotic pressure in the particles counteracting the Laplace pressure caused by the interface energy. As long as all droplets have reached the same effective pressure ($p_{\mathrm{Laplace}} - \Pi_{\mathrm{osm}}$), the particle size and its distribution does not change by Ostwald ripening, but only by droplet collisions.

(3) The surface coverage of the droplets with surfactant of an equilibrated miniemulsion is incomplete. Since the surfactant molecules on the droplets are in equilibrium with those at the water/air interface, the dispersion surface is also incompletely covered, and the surface tension of the miniemulsions is larger than the value of a surfactant saturated surface at $c_{\mathrm{surf}} > c_{\mathrm{surf}}$ (cmc). This can be checked by surface tension measurements of the miniemulsion.

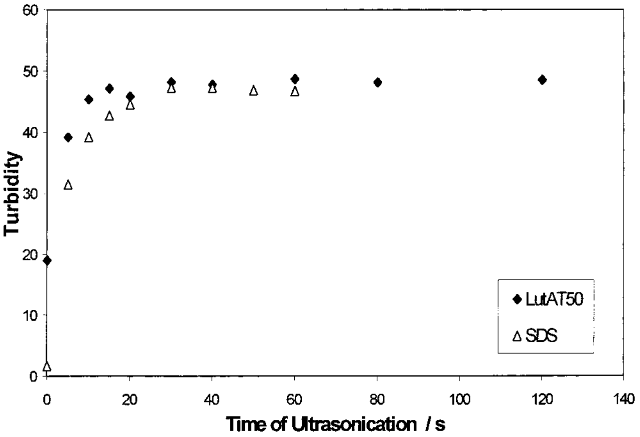

Figure 1. Turbidity during high shear miniemulsification under the described conditions.

(4) The underlying equilibrium results in typical relations between the amount of surfactant and the resulting particle size which again is related to the surface coverage. With increasing amount of the surfactant, the particle size decreases. The smaller the particles are, the higher is the coverage of the particles by surfactant.

These four points will be checked for the two different situations (nonaqueous direct and inverse miniemulsions) to ensure that the presented systems really represent polymerizable miniemulsions and less well-defined intermediate states.

(a) Polar Media. The high shear dispersion of styrene as monomer, hexadecane as hydrophobe, SDS or Lutensol AT50 as emulsifier, and formamide or glycol as dispersion media results in a steady state of turbidity which is rapidly reached. It has to be noted that the turbidity measurements using the backscattered light are indeed very sensitive to changes in particle size and particle size distributions. In the case of Lutensol AT50, the steady state is reached under the applied conditions within 20 s, whereas in the case of SDS the steady state is reached after 40 s (Figure 1). The long-term stability of the miniemulsions was checked by turbidity measurements after the miniemulsification process, and the turbidity remained constant on the time scale of hours.

For the polymerization of the monomer droplets, both AIBN or KPS as initiators were employed. In the case of the more lipophilic AIBN which was mixed to the monomer phase prior to miniemulsification, an aggregation of particles was observed. This might be due to the fact that AIBN has a high solubility in both organic phases and therefore the polymerization can be started simultaneously and uncontrolled in the droplets and in the continuous phase. The hydrophilic initiator KPS however turned out to be very suitable, since it only goes to the more polar phase and starts the polymerization controlled from this side.

Table 2 already summarizes all the data of the polymerization runs performed in polar solvents with different amounts of the standard surfactant, sodium dodecyl sulfate (SDS), and a nonionic steric stabilizer, Lutensol AT50.

It is seen from the data that SDS in formamide is far from being a good stabilizer: the size of the latex particles is larger than in water, and the particle size

Table 2. Characteristics of Styrene Miniemulsion Latexes Made in Polar Media, Where 6 g of Styrene and Different Amounts of SDS or Lutensol AT50 Were Used[b]

latex	surfactant type	surfactant amt (mg)	initiator	particle size (nm)	γ (mN m^{-1})	A_{surf}[a] (nm^2)
Miniemulsions in Water (24 g)						
StyH_2O-1	SDS	72	KPS	82	68.4	3.47
StyH_2O-9	Lutensol AT50	180	KPS	300	55.9	2.57
Miniemulsions in Formamide (24 g)						
StyFA-9	SDS	72	AIBN			
StyFA-37	SDS	74	KPS	220	51.3	1.26
StyFA-9A	SDS	125	KPS	251	51.0	0.66
StyFA-38	SDS	252	KPS	183	51.2	0.45
StyFA-39	SDS	502	KPS	188	49.8	0.22
StyFA-40	Lutensol AT50	126	KPS	253	47.5	4.34
StyFA-41	Lutensol AT50	252	KPS	138	49.8	3.98
StyFA-14	Lutensol AT50	507	KPS	71	50.9	3.89
Miniemulsions in Glycol (46 g)						
StyGly-32	SDS	52	AIBN	*c*		
StyGly-22	Lutensol AT50	500	KPS	216		1.28
StyGly-2	SDS	128	PEGA200	418		0.38
StyGly-1	Lutensol AT50	500	PEGA200	193		1.43

[a] Calculated on the base of titration experiments: 80% SDS on latexes, 20% in formamide, and 100% Lutensol AT50 on latexes. [b] Hexadecane (250 mg) was added as hydrophobe. For comparison, also data of the corresponding water-based latexes are given. [c] Aggregates.

does not decrease with increasing SDS content. This is visualized by calculating the apparent latex surface area per surfactant molecule A_{surf} from size, stoichiometric data and latex titration by surfactant. It was found from titration that 80% of the SDS is placed on the latex, whereas 20% is in the formamide phase. The calculated value of the apparent area per molecule can be as low as $A_{surf} = 0.218$ nm^2, i.e., well below the area requirement of the molecule itself. It is interesting to note that, for all compositions, the experimentally determined surface tension of the formamide latexes (see Table 2) is still above the value of a saturated SDS/formamide surface ($\gamma_{min} = 45$ mN m^{-1}), indicating that the excess of SDS is still bound to the particle. This can be speculatively attributed to SDS multilayer formation or admicellar aggregation onto particles. The difference of the behavior between water and formamide is to our understanding not due to polarity or van der Waals interaction (formamide is more polar and has a higher refractive index) but caused by a less effective solvation of the ions, which results in a lower degree of dissociation and effective charge. Therefore, the formation of miniemulsions in formamide with SDS is in principle possible, but not favorable.

On the other hand, the formation of miniemulsions with the nonionic surfactant Lutensol AT50 turned out to be very efficient. The resulting particle sizes are smaller than the corresponding ones in water. In addition, the expected dependence of particle size on the amount of surfactant is detected (see Table 2 and Figure 2). The incomplete coverage of the particles was checked by surface tension measurements, and values of 47−50 mN m^{-1} clearly indicate an incomplete coverage of the particles. The surface tension of pure formamide is $\gamma = 57$ mN m^{-1}, γ at the cmc of Lutensol AT50 in formamide is $\gamma = 39$ mN m^{-1}. This is paralleled by the high calculated A_{surf} values, indicating a low particle coverage and a very efficient use of the surfactant. The difference to the data in water[2] can be again explained by solvation effects: formamide is a better solvent for poly(ethylene oxide) than water, and the steric stabilization becomes more efficient.

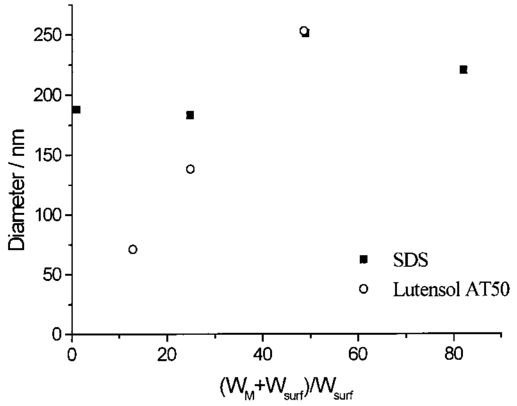

Figure 2. Dependence of the particle size on the amount of surfactant for miniemulsion reactions in formamide.

It should be also noted that the surface tension of the initial miniemulsion is also well above the value at the cmc and only slightly lower than the surface tension values of the final latexes, which is an indication that clean droplet nucleation should be the dominant initiation mechanism.

For some other concepts (such as the living radical polymerization), it would be favorable to formulate a miniemulsion in a high boiling solvent, allowing polymerization temperatures well above 100 °C without pressurizing the reaction. This is why it was also tried to use glycol as an alternative continuous phase. The data in Table 2 indicate that indeed miniemulsions can be made in glycol too, and particles as small as 193 nm diameter are accessible. Here, the observations essentially follow the patterns found for the formamide systems: it is important to select an initiator which just dissolves in one of the phases. The solubility of KPS in both the monomer and the glycol is too low to be efficient, whereas AIBN again dissolves in both phases. For glycol, the nonionic poly(ethylene oxide)-based azo-initiator PEGA200[19] turned out to be suitable. Within the solvent series (water → formamide → glycol), SDS is even less efficient, whereas Lutensol AT50 preserves a moderate activity. This is due to the fact that glycol is close to be a Θ solvent for poly(ethylene oxide).

For further application, it has to be noted that formamide and glycol latexes can easily be diluted with water, preserving the stability of the systems. This can

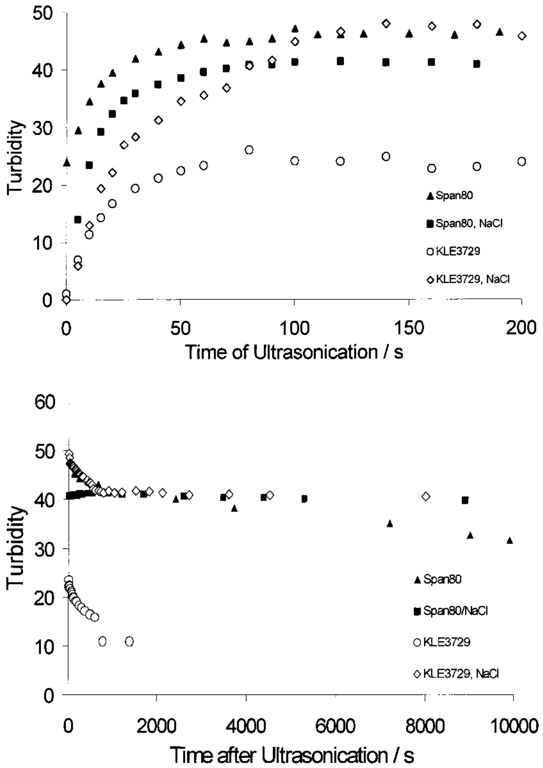

Figure 3. Turbidity measurement of water emulsions in cyclohexane with Span 80 and KLE3729: (a) during ultrasonication; (b) after ultrasonication.

also be used to characterize the latexes by diluting the reaction solutions with water, avoiding the problems of dynamic light scattering with the high viscosity solvent glycol.

(b) Nonpolar Media. For the dispersion of polar monomers in nonpolar dispersion media, surfactants with low HLB values are required. The concept of using a hydrophobe to stabilize the disperse droplets has to be adapted by adding a very lipophobic substance.

A number of surfactants was screened, including standard systems such as $C_{18}E_{10}$ and sodium bis(2-ethylhexyl) sulfosuccinate (AOT), and the nonionic block copolymer stabilizer poly(ethylene-*co*-butylene)-*b*-poly(ethylene oxide) (KLE3729) and sorbitan monooleate (Span80). KLE3729 and Span80 turned out to be the most efficient and are compared in the following experiments.

To establish the appropriate dispersion conditions, pure water (6 g) was mixed with the surfactant (750 mg) solutions in cyclohexane (24 g) and emulsified by ultrasonication. For both surfactants, a steady state of the droplet size could be reached, as revealed by turbidity (Figure 3a).

Because of the higher molecular weight and the coupled lower mobility of the surfactant molecules, the KLE3729 emulsions reach the steady state later than Span80 emulsions: sonication times of 150 s instead of about 60 s are required. After the emulsification, the turbidity of the pure water emulsions decreases, indicating the low stability of systems where the dispersed phase consists only of one pure component. The stability is lower in the case of KLE3729 than in the case of Span80. Phase separation took place within 4 h.

To obtain stable miniemulsions, the strong “lipophobe” NaCl was mixed to the water phase in order to build up an osmotic pressure in the droplets. As expected, and in accordance with a droplet fission/droplet fusion picture, the approach to the steady state of turbidity is very similar to that of the systems with salt, but after the miniemulsification, drastic stability differences are observed. In the case of Span80, the turbidity does hardly change at all over the time scale of hours, whereas in the case of KLE3729 a constant turbidity is reached after 1000 s (Figure 3b).

For inverse miniemulsions, it is not the surface between the hydrophobic dispersion and air (being already very low) which is sensitive to the surfactant distribution. Instead of that, water is added to the miniemulsions to form an under layer, and the interface tension between water and the hydrophobic miniemulsion is determined to access the surfactant coverage of the droplets.

The interfacial tension of pure cyclohexane/water was determined to be ca. 50 mN m^{-1} (see also[20]), in the case of a saturated KLE3729/cyclohexane solution, the interfacial tension decreased to 20 mN m^{-1}, being taken as the saturation value for systems containing inverse micelles. An interfacial tension of 40 mN m^{-1} for the resulting miniemulsion against water indicates the absence of micelles and incomplete coverage of the particles. This means that also the second criterion for the formation of a miniemulsion is fulfilled: the droplets show incomplete coverage by surfactant molecules. Similar interface properties were also observed for all systems based on Span80. Here, the interfacial tension at the cmc of Span80 in cyclohexane was determined to be 5.4 mN m^{-1}, whereas the water in cyclohexane miniemulsion showed an interfacial tension against water of 13.4 mN m^{-1} indicating also the incomplete coverage of the droplets.

It is summarized that both the dispersion and stability behavior and the surfactant coverage of the droplets already indicate the presence of inverse miniemulsions. For polymerization in inverse miniemulsions, a large variety of hydrophilic monomer can be used, such as hydroxyethyl methacrylate, acrylamide, or acrylic acid. Because these systems possess different solubilities in the continuous phase and influences the interfacial tensions in different ways, they are to be treated separately and are discussed in different paragraphs.

Hydroxyethyl Methacrylate. Hydroxyethyl methacrylate is a moderately hydrophilic monomer where the inverse miniemulsion polymerization process is expected to be suitable to obtain PHEMA particles. For most of the experiments cyclohexane was chosen as a continuous phase because it can be simply removed from the polymers. For universality, it was shown that hexadecane can also be chosen as the continuous phase. As initiators, PEGA200 which is soluble in the monomer phase, but not in cyclohexane, turned out to be applicable; AIBN which is mainly soluble in the cyclohexane phase could also be successfully used. KPS turned out not to be a working initiator due to solubility problems. Small amounts of water act as lipophobe, and it could be shown by turbidity measurements that such a dose increases the emulsion stability.

The characteristics of the resulting latexes are listed in Table 3. Rather small inverse latex particles in the size range between 80 and 160 nm and narrow size distributions are obtained. The systems are stable down to 1.6 wt % surfactant with respect to monomer; at lower amounts, the systems tend to coagulate.

Table 3. Characteristics of HEMA Latexes Synthesized with 3 g of HEMA

	continuous phase		surfactant		lipophobe		initiator			
latex	type	amt (g)	type	amt (mg)	type	amt (mg)	type	amt (mg)	particle size (nm)	A_{surf} (nm^2)
HEMA-15	CH	25	KLE3729	100	H_2O	142	PEGA200	100	160	11.8
HEMA-61	CH	25	KLE3729	300	H_2O	127	PEGA200	64	129	4.9
HEMA-62	CH	25	KLE3729	500	H_2O	132	PEGA200	108	102	3.7
HEMA-1b	CH	14	KLE3729	720	H_2O	90	PEGA200	120	94	2.8
HEMA-1	CH	25	KLE3729	50	H_2O	140	AIBN	60	149	25.3
HEMA-13	CH	25	KLE3729	127	H_2O	127	AIBN	60	129	11.5
HEMA-3	CH	25	KLE3729	150	H_2O	133	AIBN	64	107	11.7
HEMA-2	CH	25	KLE3729	300	H_2O	129	AIBN	62	82	7.7
HEMA-63	CH	25	KLE3729	500	H_2O	125	AIBN	60	78	4.8
HEMA-2b	HD	14	KLE3729	720	H_2O	90	PEGA200	120	84	3.1

Table 4. Characteristics of the Acrylamide Latexes

	monomer		continuous phase		surfactant			
latex	type	amt (g)	type	amt (g)	type	amt (mg)	particle size (nm)	A_{surf} (nm^2)
AAm2	acrylamide in H_2O/NaCl	3 4	CH	40	KLE3729	125	193	18.2
AAm3	acrylamide H_2O/NaCl	3 4	CH	32	KLE3729	255	142	12.1
AAm4	acrylamide H_2O/NaCl	3 4	CH	32	KLE3729	500	126	7.0
AAm13	acrylamide in H_2O/NaCl	3 4	CH	32	Span 80	1	80	0.2

Independent of the initiator, it was found that, with increasing amount of surfactant, the particle size decreases as expected. The use of AIBN as initiator results in a smaller particle size than the use of PEGA200. In the case of AIBN, stable latexes with as low as 50 mg (1.6 wt %) of surfactant can be successfully synthesized. The area per surfactant molecule, A_{surf}, decreases with decreasing particle size and follows the same trend as in the case of direct miniemulsions shown earlier.[2] This means that the surface coverage is a function of the particle size: for smaller particles more surfactant is required in order to obtain stable latexes. In the case of AIBN, A_{surf} can be even as high as 25.3 nm^2. In principle, the reaction can be started either from the continuous phase (AIBN) or directly in the monomer droplets (PEGA200). It is remarkable that the final dispersions are stable for a longer time even at that low surface coverage.

Acrylamide. For the synthesis of acrylamide in a miniemulsion polymerization process, the solid crystalline monomer has to be dissolved in water; therefore a higher amount of water was applied for the synthesis, and the continuous phase was cyclohexane. Without the addition of a strong lipophobe (NaCl), the miniemulsions after sonication show only a low stability (less than 1 h). A polymerization of such an emulsion leads to a large distribution in particle size, and because of a large fraction of large particles, the dispersion is not stable. Therefore, NaCl was added as an additional lipophobic agent to increase the stability of the miniemulsions (stable for several days). The polymerization was started by adding 100 mg of AIBN to the continuous phase after miniemulsification, and stable polymer dispersions were obtained. The resulting data of all latexes are summarized in Table 4. It is obvious that the addition of salt (enabled by the high amounts of water) has a positive effect on the formulation of the miniemulsions: already at surfactant loads as low as 1.5 wt % with respect to the dispersed phase stable latexes are obtained. The particle size is getting smaller with increasing amounts of the surfactant KLE3729. Depending on the particle size, the surface demand per surfactant molecule A_{surf} is between 18 nm^2 at low surfactant amounts (AAm2) and 7 nm^2 for higher surfactant amounts (AAm4). It is also possible to synthesize acrylamide particles in a miniemulsion polymerization process using cyclohexane and Span80 as surfactant. In this case, a much higher surfactant concentration is necessary in order to obtain stable latexes, and the use of polymeric surfactants is the superior choice.

Acrylic Acid. Acrylic acid was polymerized in the inverse miniemulsions together with 4 wt % of the cross-linking agent diethylene glycol diacrylate in order to obtain homogeneous polyelectrolyte microgels which can be also redispersed and characterized in water. However, the solubility of acrylic acid in cyclohexane is not negligible. Therefore, the solubility of acrylic acid in cyclohexane was examined by ^{1}H NMR under different conditions. The addition of water to acrylic acid already decreases the solubility of acrylic acid in cyclohexane significantly. For a formulation of a stable inverse miniemulsion a lipophile is required which can be an inorganic salt. For this purpose, we used a 1 M NaCl solution and a 5 M NaOH solution for detailed solubility studies at reaction temperature (65 °C). As seen in Figure 4, with increasing amounts of the 1 M NaCl solution the solubility of acrylic acid in cyclohexane can be significantly decreased. Using the 5 M NaOH solution, the partitioning of acrylic acid was shifted more into the water phase, and at a 2:1 ratio NaOH: acylic acid only 7% of the acrylic acid was found to be soluble in cyclohexane. NaOH not only acts as a lipophobe but also neutralizes the acid which leads to a higher hydrophilicity of the component. To minimize the water content in the synthesis, the miniemulsion polymerization was performed at an 1:1 ratio of monomer and water. The reaction was started by adding AIBN to the continuous phase after the miniemulsification. The characteristics of the resulting latexes are summarized in Table 5.

It was found that a critical surfactant amount of 2.5 wt % with respect to the monomer phase is required to prevent the formed polymer particles from aggregation

Table 5. Characteristics of Acrylic Acid Latexes Synthesized in an Inverse Miniemulsion Process Using 1 g of Acrylic Acid, 40 mg of Diethylene Glycol Diacrylate and 50 mg of AIBN

	continuous phase		surfactant		lipophobe			
latex	type	amt (g)	type	amt (mg)	type	amt (g)	particle diam (nm)	A_{surf} (nm^2)
AA8	CH	20	KLE3729	50	5 M NaOH	1	101	24.9
AA17	CH	20	KLE3729	100	5 M NaOH	1	80	15.7
AA18	CH	20	KLE3729	125	5 M NaOH	1	76	13.2

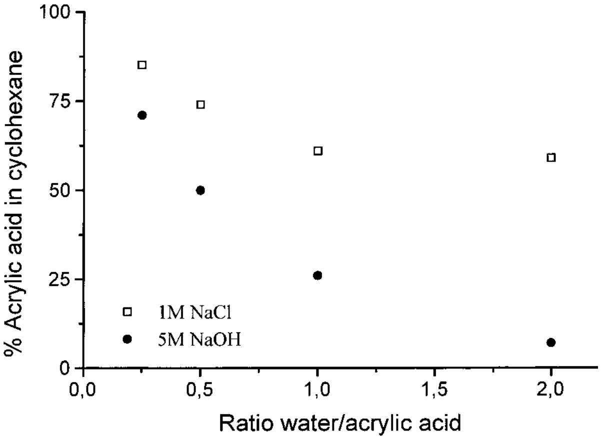

Figure 4. Partitioning of acrylic acid in cyclohexane at 65 °C under reaction conditions depending on the use of 1 M NaCl and 5 M NaOH.

and produce a stable latex of about 100 nm (latex AA8). Increasing the surfactant amount leads to smaller particles. The stabilized area per surfactant molecule, A_{surf}, is very high. In the case of low surfactant concentration, A_{surf} is 24.9 nm^2 and decreases to 13.2 nm^2 in the case of higher amount. These values are unexpectably high; i.e., the used block copolymer turned out to be a very efficient stabilizer.

The quality and the monodispersity of the particles is very good, as best seen with electron microscopy. Figure 5 shows a typical micrograph of such a latex dispersion (AA18). One can seen that the particles have a polydispersity of less than 10%, with a few rare larger species which we attribute to imperfections of the ultrasonication process in the small volumes applied. The particles slightly deform, which is due to the water added for osmotic stabilization. This example is a proof that the monomer solubility is not a serious hindrance for the miniemulsion polymerization. Since the interfacial tension of the miniemulsion and of the final latex to water are very similar to each other, it is expected that droplet nucleation is still the main initiation mechanism.

Because of the cross-linking, the particles could be dried and redispersed in water under retention of their particular identity. Here, rather monodiperse particles with a diameter of 218 nm are found; i.e., a swelling of the microgels by a volume factor of 80 occurs. This is rather typical for polyelectrolyte microgels in salt-free solutions.

The use of Span80 turned out not to be suitable to obtain stable acrylic acid latexes since monomer and the surfactant strongly interact and form complexes.

Conclusion

It was shown that the principle of aqueous miniemulsions can be transferred to nonaqueous media. In direct miniemulsions using polar media as formamide or glycol instead of water and hydrophobic monomer, the miniemulsion stability was, as in the case of the aqueous systems, obtained by a hydrophobic agent which pre-

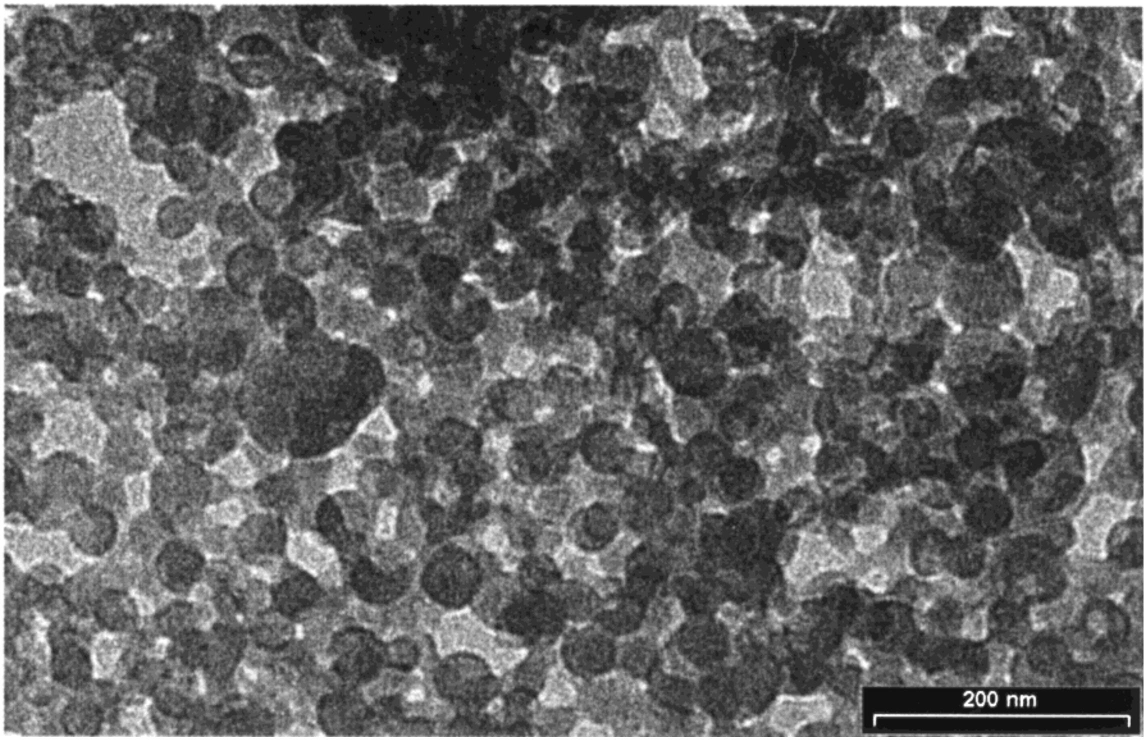

Figure 5. Transmission electron micrograph of the dried sample AA18.

vents the droplets from Ostwald ripening. It turned out that steric nonionic surfactants based on poly(ethylene oxide) tails are by far more efficient than ionic stabilizers, which is speculatively attributed to a low degree of ion solvatation and degree of dissociation in formamide. It was possible to make particles as small as 70 nm, which is unusually small for nonaqueous heterophase polymerization techniques. Surface tension measurements showed incomplete coverage of the polymer particles with surfactant.

In the case of inverse systems, hydrophilic monomers were miniemulsified in a nonpolar media, e.g., cyclohexane or hexadecane. To provide osmotic stabilized droplets, simply water or a salt were added as a "lipophobe" to the monomer phase. It was shown that such inverse miniemulsions showed long-term stability against Ostwald ripening, and the incomplete coverage of the droplets by surfactant molecules was proven by interfacial tension measurements. Rather small and narrow distributed latexes in a size range between 50 nm $< d <$ 200 nm were made of hydroxyethyl acrylate, acrylamide, and acrylic acid where nonionic amphiphilic block copolymers with poly(ethylene-*co*-butylene) tails turned out to be the most efficient stabilizer of our examination. Depending on the system, the surfactant loads can be as low as 1.5 wt % per monomer, which is very low for an inverse polymerization reaction and clearly underlines the advantages of the inverse miniemulsion polymerization technique.

As compared to classical inverse techniques such as polymerization in inverse microemulsions[21] or dispersion polymerization,[22] polymerization of inverse miniemulsions is favored by the very efficient use of surfactant and the copying process from the droplets to the particles. This leads to a homogeneous structure and composition of the resulting particles (no kinetic effects are involved). The latter feature is especially important for homogeneous cross-linking or copolymerization in inverse heterophase polymerization.

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