

Comparing emulsion polymerization of methacrylate-monomers with different hydrophilicity

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Abstract

A comprehensive experimental study concerning the influence of various types of initiator–emulsifier systems on emulsion polymerization of methacrylate monomers (2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA) and butyl methacrylate (BMA)) reveals interesting relations between initiator and surfactant hydrophilicity on the one hand and the hydrophilicity of the monomers on the other hand. For the water-soluble HEMA stable latexes are only obtained if hydrophobic initiators such as 2,2'-azobisisobutyronitrile or dibenzoyl peroxide in combination with alkyl sulfate surfactants with carbon chain lengths greater than 10 or surface active initiators of the 2,2'-azobis(*N*-2'-methylpropanoyl-2-amino-alkyl-1)-sulfonate type with alkyl chain lengths greater than 8 are employed. Stable nano size range poly(2-hydroxyethyl methacrylate) (PHEMA) particles have been prepared also by batch emulsion polymerization using ionic surface active initiators (inisurfs). The results clearly show that the formation of stable latex particles requires a proper choice of the initiator–emulsifier system regarding its hydrophilic–hydrophobic balance. The PHEMA particles prepared with surface-active initiators keep their identity and spherical shape even in the dried state whereas in the case of the other initiator–emulsifier systems complete coagulation and coalescence occurs during drying.

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1. Introduction

In aqueous heterophase polymerizations the resulting latexes are stabilized due to the existence of hydrophilic groups at the interface. Such groups can be introduced either by initiator residues, comonomers, or as in most of the practical cases by adsorbed surfactants [1]. It is important to understand that the hydrophilic–hydrophobic balance established before initiating the polymerization may change due to chemical transformations until the polymerization is complete. For example, if a polymer made of a hydrophilic monomer exhibits a lower critical solution temperature below the polymerization temperature, the polymer chain becomes hydrophobic above a certain chain length and

precipitates. This happens in the case for *N*-isopropylacrylamide for polymerization temperatures above about 32 °C as already the trimer becomes insoluble in water [2]. Although the precipitation, i.e. the transition from hydrophilic to hydrophobic is a physical change, the actual reason is the chemical conversion of the monomer. The hydrophilic–hydrophobic conditions in heterophase polymerizations are a complicated mix influenced by properties of the monomer(s) and polymer(s), the initiating species, the surface-active molecule(s), other auxiliary materials and the process variables such as temperature, feeding profiles, and hydrodynamic forces (stirring speed etc.). Consequently, the colloidal stability is governed by the same variables. The paper considers only *ab initio* emulsion polymerization in the presence of various types of stabilizers, which is generally defined as polymerization of monomers in aqueous medium in the absence of seed particles whereby the resulting polymers are water-insoluble and form finally a polymer dispersion or latex. In

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emulsion polymerization any kind of surface-active agent plays a crucial role. The most important aspect of surfactants in the context of emulsion polymerization is their ability to adsorb at interfaces where they lower the interfacial tension and impart stability to the latex particles. The adsorption behavior of surfactants on polymer particles has been frequently studied and is described in detail elsewhere [3–13]. It is convenient to express surfactant adsorption in terms of A_m , the surface area occupied per molecule. For hydrophobic or non-polar latex particles A_m is small; which means that a comparably larger number of surfactant molecules is adsorbed in contrast to more polar particle interfaces [4–7,13–16]. Consequently, for a given surfactant both the stability and the particle size differ for monomers of different polarity. The present study focuses in its major parts on the influence of the hydrophilicity or hydrophobicity of various types of surfactants (alkyl sulfates) and surface active initiators (inisurfs) of the 2,2'-azobis(*N*-2'-methylpropanoyl-2-amino-alkyl-1)-sulfonate type on ab initio emulsion polymerization of methacrylate monomers with quite different polarity (butyl methacrylate (BMA) < methyl methacrylate (MMA) < 2-hydroxyethyl methacrylate (HEMA)).

Among these monomers HEMA is exceptional because the polymerization starts as solution polymerization as this monomer is unlimitedly soluble in water whereas the polymer is not but only highly swellable. The Flory–Huggins interaction coefficient for PHEMA–water and PHEMA–HEMA is about 0.8 and 0.57 at 25 °C, respectively [17]. These values indicate that water only swells the polymer but the monomer dissolves it. Both values increase with increasing polymer volume fraction and thus, phase separation takes place. PHEMA is in the dry state a hard and brittle polymer with a glass transition temperature of about 86 °C [18], but soft and flexible in the swollen state. It is swellable in water and aqueous electrolyte solutions to a degree of about 50% by weight but in sodium hydroxide solution up to 150% [19]. Thus, polymerization of HEMA in aqueous media, where HEMA is not only the monomer but also a co-solvent, possesses all features of dispersion polymerization. That is, the reaction system is homogeneous before starting the chain growth and becomes heterogeneous as the polymer precipitates with increasing conversion [1]. Consequently, 'classical' emulsion polymerization of HEMA with the goal to prepare PHEMA-particles in the nanometer size range faces a lot of problems as the size of the polymer particles typically prepared in dispersion polymerizations is in the μm -size range. On the contrary, suspension polymerization is state of the art for the preparation of monodisperse PHEMA particles in the size range of a few hundreds of micrometers for biomedical applications [20]. There are few papers describing the use of HEMA as comonomer in emulsion polymerization in order to hydrophilize particle surfaces and to improve latex stability [21–28]. Some papers describe also the controlled polymerization of HEMA by atom transfer radical

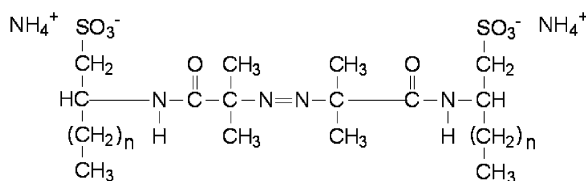
polymerization [29,30]. But only recently one research group succeeded in the preparation of PHEMA particles in a size range of about 100 nm using sodium dodecyl sulfate and 2,2'-azobisisobutyronitrile (AIBN) as stabilizer and initiator, respectively [31,32]. According to these results the experimental conditions regarding initiator and emulsifier (type and concentration) as well as stirring speed are very crucial. For instance, the authors describe that latex formation was not observed if potassium peroxydisulfate (KPS) as water-soluble initiator, or poly(vinyl alcohol) as sole stabilizer, or a high monomer content was used [32]. Furthermore, the authors point out the importance of the stirrer speed as they obtained best results at a stirrer speed of 100 rpm. A recipe published by Chu et al. [31] was the starting point for the present study with the aim to get more information concerning the conditions to get stable PHEMA-nanoparticles. Such nanoparticles might be useful for various applications or investigations where hydrophilic and biocompatible nanoparticles are required such as for model investigations of phagocytosis [33] or may be can replace micrometer-sized PHEMA particles (cf. [20,34] and references therein). Particularly, various kinds of initiators (hydrophilic, hydrophobic, and surface-active ones) and sodium alkyl sulfate emulsifiers with variable hydrophobic chain length (varying hydrophilicity or hydrophobicity) have been investigated. It is necessary to mention that inisurfs impart persistent stability to the particles as the surface-active radicals are covalently attached to the particles. This is a clear demarcation to conventional system consisting of separate initiators and surfactants as their behavior is governed by the adsorption–desorption characteristic of the surfactant.

Moreover, the different hydrophilicity of the monomers considered, MMA and BMA has a solubility in water of about 159 and 4 mM, at room temperature, respectively [35], might cause differences in the particle nucleation mechanism and hence, an interesting question is whether or not the experimental results obtained can be consistently explained with only a single mechanism.

2. Experimental information

2.1. Materials

HEMA from Acros was purified by passing it through a column containing activated neutral aluminium oxide (Sigma Aldrich). MMA and BMA from Sigma Aldrich were distilled under reduced pressure to remove inhibitor and stored in a refrigerator. Prior to use the monomers were checked regarding oligomer formation during storage by adding a drop into an excess of methanol. Only oligomer free monomers were used. The surface-active initiators of the 2,2'-azobis(*N*-2'-methylpropanoyl-2-amino-alkyl-1)-sulfonate type as depicted in Formula 1 were prepared via a modified Ritter reaction between the corresponding



Formula 1. Structure of the inisurfs; $n=2, 5, 7, 11, 13$ (the alkyl chain length of the α -olefins is $C_n=n+3$).

α -olefin, AIBN, and fuming sulfonic acid as described in Refs. [36,37] and employed as the ammonium salts.

The homologous series of alkyl sulfates with different carbon atom numbers (C_n) was prepared as described in Ref. [38]. The water was taken from a Seral purification system (PURELAB Plus™) with a conductivity of $0.06 \mu\text{S cm}^{-1}$ and de-gassed prior to use for the polymerizations. AIBN from Fluka and dibenzoyl peroxide (BPO) from Aldrich were both recrystallized from methanol before use and preserved in a refrigerator. Potassium peroxydisulfate from Fluka was reagent grade and used as received.

2.2. Characterization techniques

All latexes were characterized regarding the solids content with a HR 73 Halogen Moisture Analyzer (Mettler Toledo, Gießen, Germany) and the average particle size with dynamic light scattering with a NICOMP particle sizer (model 370, NICOMP particle sizing systems, Santa Barbara, California, USA). From the solids content (FG in %), the intensity weighted average particle size (D in nm), and the density of the polymer (ρ_p) the stabilizer efficiency (E in $\text{cm}^2 \text{g}^{-1}$ that is particle surface per g of stabilizer) was calculated according to Eq. (1), where W is the amount of water and S the amount of surfactant (either sodium alkyl sulfates or surface active initiators). Note, that the so calculated efficiency is not a material constant but a good measure to characterize the performance of the stabilizer for a particular procedure. For these calculations the bulk polymer densities at room temperature were used thus neglecting the influence of swelling of the particles with water and cross-linking.

$$E = \frac{W}{S} \times \frac{\text{FG}}{100 - \text{FG}} \times \frac{6}{\rho_p D \times 10^{-7}} \quad (1)$$

Another note is necessary regarding the solids content. A low value of FG does not indicate a low conversion because all the coagulum was removed by passing the dispersion through a pore 1 or 2 sintered glass frit. Consequently, FG is much more a measure of the latex yield and/or the stabilizing ability of the particular recipe. The latex yield (X_{latex}) was calculated according to Eq. (2) from the solids content, the auxiliaries content (HG), and the theoretical polymer content (PG_0). HG is the weight fraction (in %) of all additives in the recipe except the monomer.

$$X_{\text{latex}} = \frac{\text{FG} - \text{HG}}{\text{PG}_0} \times 100 \quad (2)$$

Transmission electron microscopy (TEM) was used in order to investigate the shape and morphology of the PHEMA particles. TEM was performed with a Zeiss EM 912 Omega microscope operating at 100 kV. For TEM the solids content of the latexes was adjusted to about 0.5% and a suspension preparation technique were employed to deposit the particles on the grid.

Ultrafiltration was carried utilizing YM1 membranes (Amicon, Inc. Beverly, MA, USA) with a molecular cut-off 1000 g mol^{-1} which is well above the molecular weight of the stabilizers. Distilled water was refilled and the ultrafiltration continued as long as the conductivity of the filtrate was constant.

2.3. Polymerizations

To monitor the influence of the different initiators, stabilizers and inisurfs batchwise emulsion polymerizations were conducted either with HEMA, MMA or BMA as monomer in a 250 ml all-glass reactor (diameter 6.5 cm and height 15 cm). The reactor was equipped with cross-arm paddle stirrer (3 arms 4 cm in length rotated at 90° in a distance of 2 and 2 cm apart from the reactor bottom), reflux condenser, nitrogen inlet and outlet, heating jacket to control the temperature, and a valve on the bottom to remove the latex. Particularly, two sets of experiments have been carried out. The first study concerned the influence of the chain length of alkyl sulfate emulsifiers with either hydrophilic (KPS) or hydrophobic initiators (AIBN, BPO) with the following recipe at 60°C : 0.2 g of initiator, 0.35 g of surfactant (S), 185 g of water (W), and 15 g of HEMA, stirrer speed 100 rpm. In the second study surface active initiators (cf. Formula 1) with variable hydrophobic chain length have been used as combined initiating and stabilizing system with the following recipe at 90°C : 0.5 g of inisurf (S), 250 g of water (W), and 3 g of HEMA, stirrer speed 45 rpm.

Due to the low stirrer speeds the MMA and BMA are not completely emulsified but a bulky monomer layer rests on top of the reaction mass. After the polymerizations and before any characterization of the latexes the coagulum was removed by passing the dispersion through a pore 1 or 2 sintered glass frit.

It is important for the subsequent discussion to emphasize that the concentration of both the alkyl sulfates and the inisurf is at C_n -values between 12 and 14 above the critical micelle concentration (CMC). For the alkyl sulfates and the inisurfs investigated the CMC is in between about 1 M (C_6) and 10^{-4} M (C_{18}) [39] and about $4 \times 10^{-2} \text{ M}$ (C_8) and $3 \times 10^{-4} \text{ M}$ (C_{16}) [40], respectively. This is only an estimate based on CMC data at 25°C which, however, should be reasonable as well at the polymerization temperatures as on the one hand the CMC of ionic

surfactants generally increases only slightly with increasing temperature [41] and on the other hand the dependence of the CMC on the alkyl chain length is much steeper than that of the concentration. A further uncertainty arises from the fact that all these CMC values refer to pure water whereas during the polymerizations the continuous phase is a monomer in water solution of different composition depending on the hydrophilicity of the particular monomer.

3. Results and discussions

The data reported in Table 1 prove the enormous influence of the kind of initiator on the emulsion polymerization of HEMA with SDS as emulsifier. On the contrary to more hydrophobic monomers the hydrophobic initiators lead in this case to much better polymerization results, that is much less coagulum and smaller particles, than the hydrophilic KPS. A low value of the solids content does not mean automatically a low conversion but is much more an expression of the larger amount of coagulum formed, which corresponds according to Eq. (2) to a low latex conversion. Particularly, the average particle size and the solids content together characterize the initiator emulsifier system (IES) regarding its stabilizing capability. High solids content together with low particle size characterize an IES with a high stabilizing ability (cf. Eq. (1)).

There are several possibilities to explain the poor polymerization results obtained with KPS. One reason might be the higher polarity of the particle surface due to the incorporated sulfate groups causing larger A_m -values and less stabilizer molecules to be adsorbed. Differences in the size of the particles at the end of the nucleation period can also explain the different efficiencies.

Obviously, the preparation of nanometer-sized PHEMA particles requires hydrophobic initiator residues in the growing polymer molecules causing chain aggregation at lower degree of polymerization as elementary step during particle nucleation. As long as the chain length of the PHEMA chains is not too high these chains contribute to stability additionally to the surfactant molecules. This is obviously the mirror-scenario compared with polymerization of hydrophobic monomers such as styrene, MMA and BMA with hydrophilic initiators where the hydrophobicity of the growing oligomer chains causes aggregation but the hydrophilic initiator residues contribute additionally to the surfactant molecules to the stability of the particles. These

considerations do not mean that the particle nucleation mechanism is generally different between the water-soluble HEMA and the more hydrophobic MMA and BMA. The aggregative nucleation mechanism, based on ideas adopted from the classical nucleation theory as described in Refs. [42–44], can consistently explain the results despite the quite different water solubility of the monomers. Such a consistent explanation is practically impossible by means of the micellar nucleation mechanism. It is to note, that at the given recipe the surfactant concentration is for C_n greater and smaller than 12 above and below the CMC, respectively. Obviously, the presence or absence of micelles has no significant influence on the average latex particle size but the polarity of the surface and the adsorption–desorption behavior of the surfactants does.

It is to emphasize that the results for HEMA regarding the influence of the nature of the initiator are completely different compared with hydrophobic monomers such as styrene. In the latter case hydrophilic and hydrophobic initiators behave very similar regarding latex yield [45] and even the kinetics of the polymerizations differ not that much as it might be expected [46].

The influence of the hydrophobicity of alkyl sulfate surfactants on the polymerization was investigated with AIBN as initiator. Figs. 1 and 2 shows how the average particle diameters and the efficiencies change for all three monomers in dependence on the alkyl chain length of the surfactants (C_n). These two values strongly depend on both the hydrophilicity of the monomer and the alkyl chain length of the stabilizer. Regarding the average particle size it is to note that it decreases with increasing surfactant chain length (increasing hydrophobicity or increasing surface activity) for MMA and BMA but increases for HEMA.

An explanation of these experimental facts can be given again by means of the adsorption–desorption behavior of the surfactant molecules. The longer the alkyl chain length the stronger is the adsorption of the surfactant molecules due to their enhanced hydrophobicity for PBMA and PMMA particles. Parallel to the decrease in the average particle size takes place an increase in the efficiency (cf. Fig. 2). For the hydrophilic PHEMA particle interface the situation is completely different as the average particle size increases with increasing surfactant hydrophobicity. Furthermore, it needs a certain minimum hydrophobicity to get stable, nanometer-sized latex particles. This is reached if $C_n > 10$ as for the other stabilizers complete coagulation takes place. The increase in the average size of the PHEMA-particles with increasing alkyl chain length of the surfactants is

Table 1
Influence of the initiator hydrophobicity on aqueous heterophase polymerization of HEMA

Initiator	FG (%)	X_{latex} (%)	D (nm)	E (cm ² g ⁻¹)
AIBN	7.53	97.0	88.8	2.26×10^7
BPO	7.86	100.0	94.3	2.22×10^7
KPS	0.87	8.0	248.2	8.70×10^5

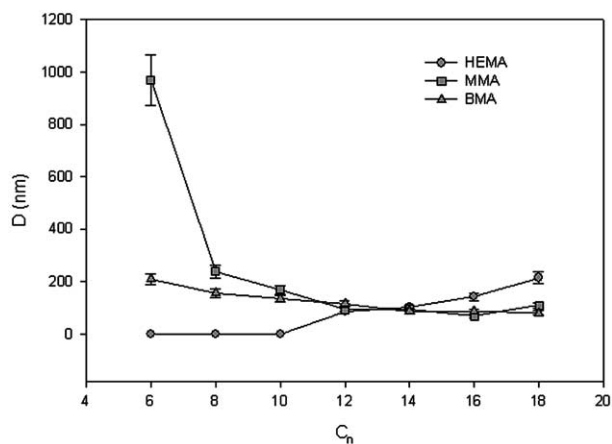


Fig. 1. Average particle size in dependence on the chain length of alkyl sulfate surfactants, initiator AIBN.

caused by the hydrophilicity of the particle surface as the surfactants tails with increasing carbon atoms gain stepwise more and more energy by mutual interaction than by adsorption. For $C_n > 14$ surfactant self-assembly dominates against adsorption. The other surfactants with $C_n < 10$ prefer to stay in solution instead of being adsorbed thus leading to complete coagulation. Obviously, for the more hydrophobic PBMA and PMMA interfaces adsorption of the surfactants can compete energetically with self-assembly and dissolution of the alkyl sulfates. This scenario finds its expression also in the dependence of the efficiency on C_n as shown in Fig. 2. This statement holds for the course of the curves but not necessarily also for the comparison of the E -values between the different monomers as the existence of a free monomer phase on top of the reaction mixture due to the low stirring rate favors bulk polymerization and hence a decrease in the efficiency with increasing hydrophobicity of the monomers. This is the reason that the absolutely highest efficiencies are obtained for HEMA polymerizations in the presence of C_{12} and C_{14} alkylsulfate surfactants as considering only the surfactant adsorption–desorption

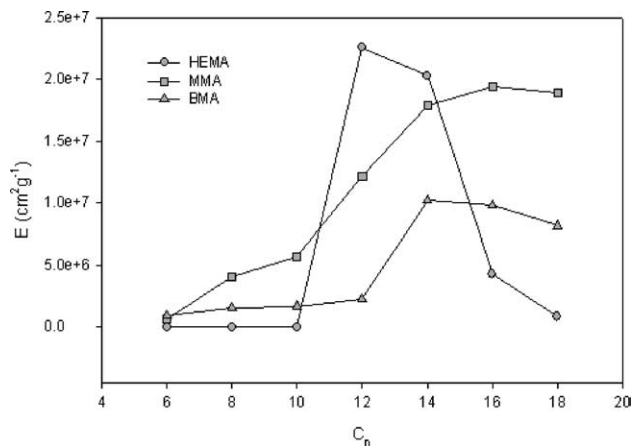


Fig. 2. Stabilizer efficiency in dependence on the chain length of alkyl sulfate surfactants, initiator AIBN.

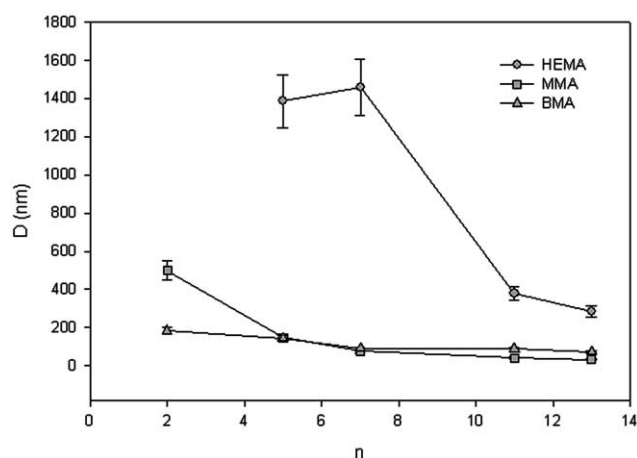


Fig. 3. Average particle size in dependence on the alkyl chain length of inisurfs ($C_n = n + 3$).

behavior one would expect higher efficiencies for the more hydrophobic monomers.

Also for the inisurfs employed the average particle size and the efficiency strongly depend on the hydrophobicity of both the monomers and the surface-active radicals as shown in Figs. 3 and 4. Also in this case the particular dependencies for the hydrophilic HEMA are quite different compared to those obtained with the alkyl sulfate surfactants. The efficiency increases steadily (cf. Fig. 4) and the average particle size has maximum values at C_n -values of 8 and 10 (cf. Fig. 3) for the water-soluble monomer. The polymerizations of MMA and BMA lead to the expected results, which means that the average particle size and the efficiency decreases and increases with increasing C_n -values of the inisurfs, respectively.

The peculiarity of HEMA in combination with the inisurfs points to an interesting behavior in the course of the polymerization. The inisurfs affect both the nucleation and the stabilization of the particles. Changing C_n causes a change in the hydrophobicity of the PHEMA end groups and thus, C_n influences directly the primary aggregation process.

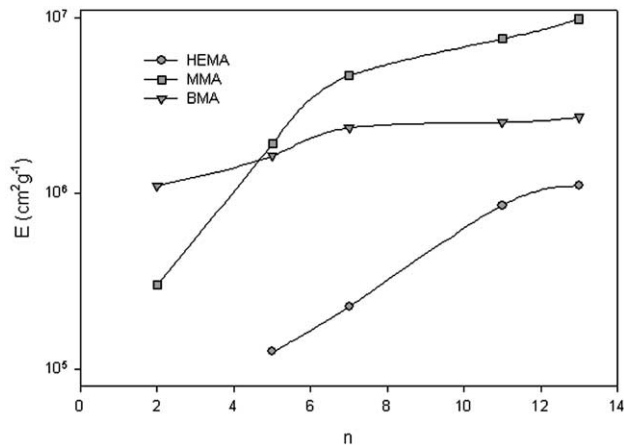


Fig. 4. Stabilizer efficiency in dependence on the alkyl chain length of inisurfs ($C_n = n + 3$).

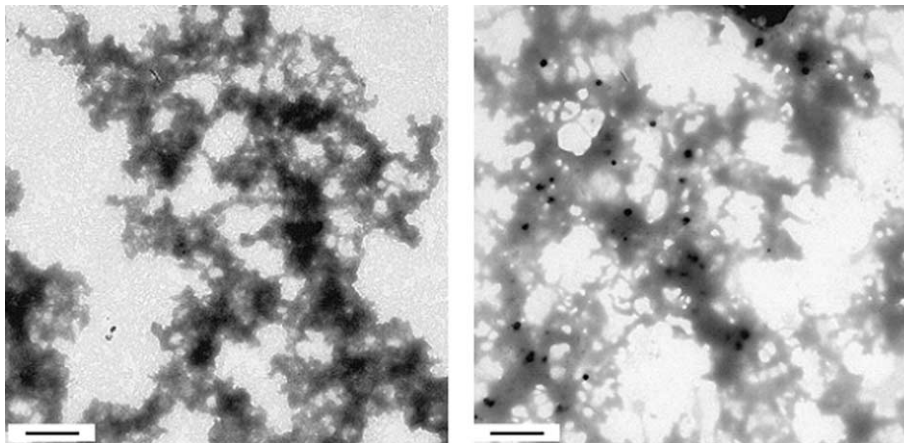


Fig. 5. TEM pictures of dried PHEMA latex prepared with AIBN (right side) and BPO (left side) as initiator and sodium dodecyl sulfate as stabilizer; suspension preparation technique to prepare the samples for TEM; the bars indicate 1000 nm in either case.

Increasing C_n should lead to the formation of a higher concentration of smaller particles as verified by the experimental results (cf. Fig. 3). Moreover, each new polymer chain contributes to stability as it contains a stabilizing (surface active) end group. On the other hand the adsorption is influenced as described above. Additionally, the adsorption might be favored compared to the other IES as the hydrophobic domain and the adsorbing moiety are chemically identical and also have the same C_n . This behavior is indeed observed experimentally as proven by a comparison of the efficiency data in Figs. 2 and 4 where both initiator–emulsifier systems show the opposite behavior.

Another peculiarity of PHEMA particles, which is observed at higher polymer concentration such as during fortification of the latexes, is the so-called ‘syneresis’. This means during drying of the dispersion phase separation takes place as water is expelled from the swollen particles with increasing solids content. Under such conditions the only weakly adsorbed surfactants can easily desorb and the syneresis pressure causes particle coagulation/coalescence. This happens also during sample preparation for TEM by

the so-called suspension preparation technique and consequently, the PHEMA particles prepared with conventional initiator–emulsifier combinations cannot be observed unless freeze-fracture techniques are employed. The TEM pictures as shown in Fig. 5 of the PHEMA latexes prepared with sodium dodecyl sulfate ($C_n=12$) as stabilizer and hydrophobic initiators prove this conclusion as no single particles are visible but typical coagulation structures whereas dynamic light scattering gave intensity weighted diameters smaller than 100 nm.

In contrast to common surfactants, which can desorb completely inisurfs cannot as a corresponding portion of them is covalently attached to the polymer. Consequently, TEM pictures after suspension preparation of PHEMA latexes prepared with inisurfs show single particles as it is proven for two different inisurfs in Fig. 6.

4. Summary and conclusions

In conclusion, these experimental studies reveal

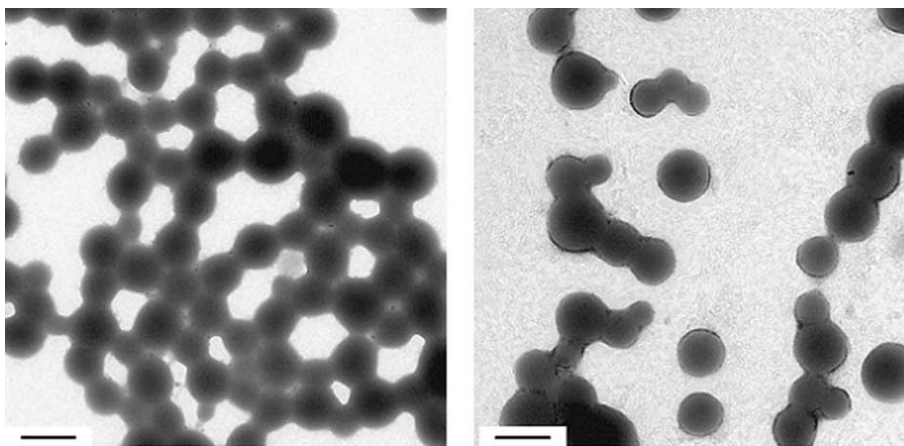


Fig. 6. TEM pictures of dried PHEMA latexes prepared with inisurfs with two different C_n -values; left: $C_n=14$, right: $C_n=16$; suspension preparation technique to prepare the samples for TEM; the bar indicates 500 nm in either case.

interesting relations between the hydrophilicity of both the monomers and the initiator–emulsifier system and the colloidal properties of the resulting latexes. The preparation of latex particles of hydrophilic monomers such as HEMA with diameters in the range of 100 nm requires well-balanced conditions regarding the hydrophobicity of the stabilizing system ($C_n=12$ or 14) in combination with hydrophobic initiators or the application of surface-active initiators. In contrast to the more hydrophobic PBMA and PMMA particles surfactant adsorption competes energetically in the case of PHEMA particles with the dissolution in the continuous phase ($C_n < 10$) and self-assembly ($C_n > 14$). The results regarding the average particle sizes can only be explained consistently with the aggregative particle nucleation mechanism [42–44] and an emulsifier adsorption strongly dependent on the polarity of the particle surface.

PHEMA particles prepared with ionic inisurfs keep their identity even during drying so that for the first time TEM pictures of spherical PHEMA particles in the nanometer size range have been obtained. Obviously, the covalently attached surface-active groups are able to counteract the syneresis pressure due to electrostatic repulsion.

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