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On the role of hydrophilicity and hydrophobicity in aqueous heterophase polymerization

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Abstract

This paper reports on experimental results of aqueous heterophase polymerizations with monomers of quite different solubility in water ranging from the water-soluble 2-hydroxyethyl methacrylate to lauryl methacrylate with solubility in water of only about 10^{-4} mM. A calorimetric study revealed the strong influence of both the hydrophilicity of the monomer and the stirrer speed on the rate of polymerization in the absence of surfactants. In order to obtain maximum latex yield and high efficiency (which is a measure considering colloidal properties, polymerization recipe, and polymerization parameters) the initiator–surfactant combination must be properly chosen in dependence on the hydrophilicity of the monomer. Results are presented for sodium alkyl sulfates or disodium-*N*-stearoyl-L-glutamate as surfactant and potassium peroxodisulfate, or poly(ethylene glycol)-azo- compounds, or 2,2′-azobis(*N*-2′-methylpropanoyl-2-amino-alkyl-1)-sulfonates as initiators.

Keywords: Inisurf; Surfactant-free; Initiator–surfactant combination

1. Introduction

Any heterophase polymerization is characterized by changing heterogeneity and dispersity during almost the entire reaction. Heterogeneity means the coexistence of different phases and is a qualitative feature, which implies that phase boundaries are of importance. Contrary, dispersity is a quantitative measure that characterizes the degree of division of the heterophase system. It is defined as the reciprocal average characteristic length scale. Generally, the coexistence of two immiscible phases requires a balanced relation between lyophilic and lyophobic interactions or between hydrophilic and hydrophobic interactions as in the particular case of aqueous heterophase polymerizations. Heterogeneity and dispersity together cause an energetic characterization of a dispersed system that is the existence of an interfacial tension between coexisting phases and an interfacial free energy (interfacial tension times interfacial area). It is straightforward that with increasing dispersity interfacial effects become more and more important. Also, the interface is responsible for all peculiarities, for all pro's and con's of heterophase polymerizations. In this sense both the hydrophilicity and the hydrophobicity of all recipe components are crucial for an understanding of aqueous heterophase polymerizations. Hydrophobic substances are defined as only sparingly soluble or insoluble in water [1] and hence, keeping them in a dispersed state requires a proper stabilization by hydrophilic components, which can be either surface active molecules, or hydrophilic polymers, or hydrophilic parts in the polymer chains arising from initiator residues, comonomers, or chain transfer reagents.

The initial state of a heterophase polymerization must not necessarily be colloidal in nature but at least during the reaction particles form as the polymer is insoluble in the continuous phase. In the course of heterophase polymerization the hydrophilic–hydrophobic balance established before initiating the polymerization may change due to

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chemical transformations until the final state is reached. Thus, the hydrophilic–hydrophobic condition during heterophase polymerization is 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.). And so is the situation regarding colloidal stability governed by the same variables.

The primary aim of this paper is to report and to compare experimental results of ab initio batch heterophase homopolymerizations with monomers of quite different solubility in water. The following monomers were included in the investigations, where C_W is their solubility in water at 25 °C: 2-hydroxyethyl methacrylate (HEMA, $C_W = \infty$) [2], methyl methacrylate (MMA, $C_W = 150$ mM) [3], styrene (STY, $C_W = 1.68$ mM) [3], *tert*-butyl styrene (TBS, $C_W \sim 10^{-2}$ mM) (estimated according to [4]), and lauryl methacrylate (LMA, $C_W \sim 10^{-4}$ mM) (estimated according to [4]). Special emphasis is placed on the conditions of preparation of the initial monomer emulsions (stirrer speed and kind of comminution), on the elaboration of experimental conditions to get high latex yields with very hydrophilic and very hydrophobic monomers, on the kind of initiator, and on the kind of stabilizer.

2. Experimental and analytical information

2.1. Materials

The monomers MMA and STY (both from Sigma-Aldrich) were distilled under reduced pressure before use. HEMA, TBS, and LMA were passed over neutral alumina (Sigma-Aldrich) in order to remove inhibitors according to a procedure described in Ref. [5]. Sodium dodecylsulfate (SDS) from Karl Roth GmbH (Karlsruhe, Germany), disodium-*N*-stearoyl-L-glutamate (DSNSG) from Anjinomoto Co., Inc., and potassium peroxodisulfate (KPS) from Sigma-Aldrich were used as received. 2,2′-Azobisisobutyronitrile (AIBN) from Fluka and benzoyl peroxide (BPO) from Sigma-Aldrich were both recrystallized from methanol before use. Stabilizers of the homologous series of alkyl sulfates with different carbon atom numbers were prepared as described in Ref. [6]. The surface-active initiators (inisurfs) of the 2,2′-azobis(*N*-2′-methylpropanoyl-2-amino-alkyl-1)-sulfonate type (AAS) were prepared as described in Ref. [7]. Symmetrical poly(ethylene glycol)-azo initiators (PEGA) with a molecular weight of the poly(ethylene glycol) chains (PEG) indicated by the subsequent number (PEGA200 up to PEGA4000) were prepared as described elsewhere [8]. The water for all experiments was taken from a Seral purification system (PURELAB Plus™) with a conductivity of 0.06 μS cm^{-1} and degassed prior to use.

2.2. Polymerizations

The batchwise heterophase polymerizations were carried out with styrene as the monomer in a 100 ml all-glass reactor. The reactor was equipped with stirrer, reflux condenser, nitrogen inlet and outlet, heating jacket to control the temperature, and a valve on the bottom to remove the latex. The standard procedure was as follows: 10 g of the monomer, 35 g of water, and 0.1 g of the stabilizer were premixed in the reactor during heating-up to reaction temperature (80 °C). Injecting the desired amounts of initiator dissolved in typically 5 g of water started the polymerizations. The initiator concentration was 30 mM for all experiments. For PEGA initiators with PEG chains of higher molecular weights the portion of water for preparing the initiator solution was correspondingly increased.

Besides the above standard procedure, some polymerizations were also conducted in a reaction calorimeter CPA200 (ChemiSens AB, Lund, Sweden). Reaction calorimetry is suited to measure directly the polymerization rate by means of the heat flow (HF). Details of reaction calorimetry of heterophase polymerization can be found elsewhere [9–11]. For the runs in the calorimeter the procedure was the same as described for the glass reactors except that the amounts of all ingredients were doubled.

The miniemulsion polymerizations have been carried out as described in Ref. [12]. 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. Consequently, the solids content (FG) is not only a measure of the conversion but corresponds much more inversely to the amount of coagulum formed during the polymerization. From the solids content a latex yield (X_{latex}) is calculated, which is the ratio of the actual polymer content and the theoretically possible polymer content.

From the solids content (FG in %), the intensity weighted average particle size (D_i in nm), and the density of the polymer (ρ_p) the stabilizer efficiency (E in $cm^2\,g^{-1}$ that is particle surface per gram of stabilizer) was calculated according to Eq. (1), where W is the amount of water and S the amount of stabilizer. For stabilizer-free polymerizations E is related to the amount of initiator and S in Eq. (1) is replaced by the mass of initiator (I). Note that the so calculated efficiency is not a material constant but a good measure to characterize the performance of a particular heterophase polymerization. For the calculations value $\rho_p = 1.05$ g cm^{-3} was used for all polymers except poly-HEMA ($\rho_p = 1.289$ g cm^{-3}) thus neglecting the influence of swelling of the particles with water [13]

$$E = \frac{W}{S} \times \frac{\mathrm{FG}}{100 - \mathrm{FG}} \times \frac{6}{\rho_p D_i \times 10^{-7}} \qquad (1)$$

2.3. Characterization methods

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 (intensity weighted average particle diameter—D_i) with a NICOMP particle sizer (model 370, NICOMP particle sizing systems, Santa Barbara, California, USA). Molecular weight distributions were determined by gel permeation chromatography (GPC) and used to calculate weight and number average molecular weights (M_w, M_n). GPC was carried out by injecting 100 μl of about 0.15 wt% polymer solutions (solvent tetrahydrofuran) through a teflon-filter with a mesh size of 450 nm into a Thermo Separation Products set-up being equipped with UV (TSP UV1000) and RI (Shodex RI-71) detectors in THF at 30 °C with a flow rate of 1 ml/min. A column set was employed consisting of three 300×8 mm columns filled with a MZ-SDplus spherical polystyrene gel (average particle size 5 μm) having a pore size of 10^3, 10^5, and 10^6 Å, respectively. This column set allows a resolution down to molecular weights less than 500 g mol^{-1}. Molecular weights and molecular weight distributions were calculated based on polystyrene and poly(methyl methacrylate) standards, respectively.

3. Results and discussions

Although all main monomers for aqueous heterophase polymerizations are typically hydrophobic in nature (according to the above definition) the water phase kinetics and also the limited water solubility of the monomers plays a crucial role during the reaction (cf. [14,15]). For instance, it is known since decades that the rate of polymerization for vinyl acetate ($C_w \sim 250$ mM) is only slightly increasing with increasing soap concentration, whereas for STY the rate jumps in the vicinity of the critical micelle concentration [16]. Furthermore, the initial polymerization rate in ab initio polymerizations during the period of particle formation is directly correlated with C_w. Thus, it might be possible that for some monomers such as TBS or LMA the solubility in water is even too low to allow surfactant-free polymerizations. The kinetic data presented in Figs. 1–3 seem to confirm this idea as the heat flow, which is a measure of the monomer conversion, detected in calorimetric investigations of emulsifier-free (e-free) polymerizations is directly proportional to the water solubility of the monomers at given other experimental conditions.

The results depicted in Figs. 1 and 2 clearly prove the influence of the stirrer speed on the rate of polymerization for all the monomers. Increasing stirrer speed from 300 to 1200 rpm leads to a detection of heat flow signals also for the monomers with low water solubility such as TBS and LMA.

Moreover, the comparison of the heat flow–time curves in Figs. 1 and 2 shows that also the rate of polymerization for MMA and STY is influenced by the stirrer speed. The general conclusion can be drawn that for surfactant-free heterophase polymerizations in aqueous media the rate of polymerization is the higher the higher the stirrer speed. This statement is even true for MMA although the main heat flow peak is clearly shifted towards longer times for stirrer speed of 1200 rpm but the reaction is finished already in almost half of the time. The general experimental observation that the rate of polymerization is increased at higher stirrer speeds can be explained with smaller droplet sizes [17]. Smaller monomer drops can act two-fold in heterophase polymerizations. First, according to the Laplace and Kelvin relations smaller monomer drops might be more soluble than larger ones in the continuous phase [18]. Second, smaller drops mean a larger drop interface and might cause initiation of the polymerization directly inside the drops due to a higher probability of radical entry from the continuous phase [19]. This might be atleast partially the case for TBS as monomer, where average particle sizes in the micrometer range were obtained (cf. Table 1) For the reaction systems with smaller drop sizes another nucleation

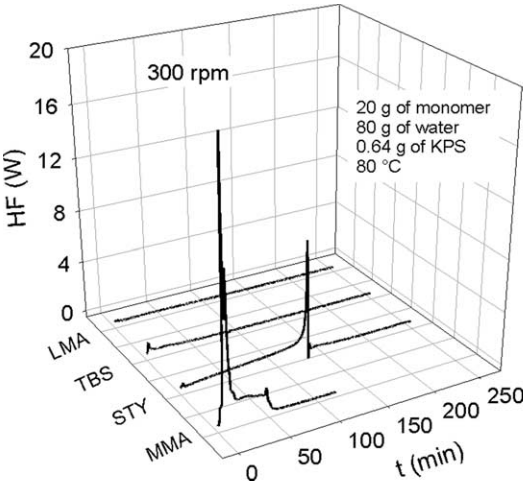


Fig. 1. Heat flow-time curves for e-free polymerizations of MMA, STY, TBS, and LMA at a stirrer speed of 300 rpm.

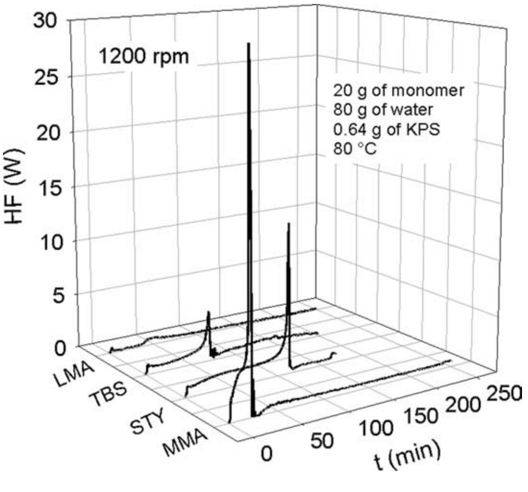


Fig. 2. Heat flow-time curves for e-free polymerizations of MMA, STY, TBS, and LMA at a stirrer speed of 1200 rpm.

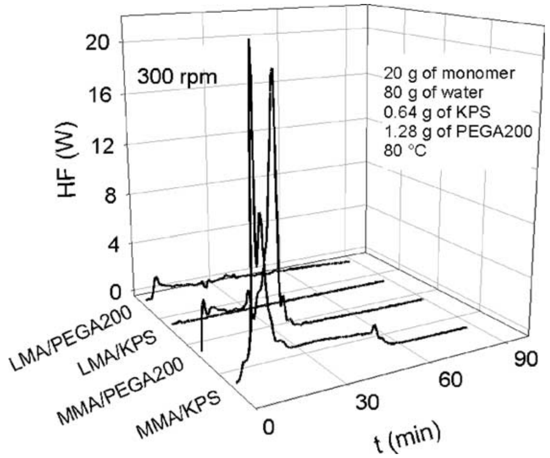


Fig. 3. Heat flow–time curves for e-free polymerizations of MMA and LMA at a stirrer speed of 300 rpm with different initiators.

mechanism is more likely as comminution by ordinary mechanical stirring is not intense enough to generate a huge portion of submicron-sized droplets.

If instead of KPS a less hydrophilic initiator is used such as PEGA200, which is due to the properties of poly(ethylene glycol) soluble in both the aqueous and the monomer phase especially at elevated temperatures [20], the observed heat flow–time curves possess different profiles as exemplary shown for MMA and LMA in Fig. 3. Despite the different water solubility of the monomers the reactions starts in any case almost immediately after initiator injection. Interestingly for MMA the maximum in the heat flow is shifted towards the end of the reaction if PEGA200 is used instead of KPS.

Calorimetry measures directly the heat development during the polymerization, which to the absolutely major part arises from monomer conversion (heat release due to splitting of the monomeric double bond) and hence, the data summarized in Figs. 1–3 does not contain direct information regarding the colloidal state of the reaction mixture. In the sense of the above discussion regarding heterogeneity and dispersity of colloidal systems it is wise to characterize the performance of a particular recipe in heterophase polymerization by the average particle size, the latex conversion, and the efficiency as defined by Eq. (1). The average particle size is the reciprocal quantitative measure of dispersity and the latex conversion the direct quantitative measure of heterogeneity that is, the extent of changing the starting emulsion into colloidal polymer dispersion. The efficiency combines both values and thus allows a quantitative comparison between different recipes and procedures. The data detailed in Table 1 clearly prove the influence of both the water solubility of the monomers and the stirrer speed on the average latex particle size and the latex yield in e-free aqueous heterophase polymerizations.

Table 1
Latex yield and average hydrodynamic particle diameter surfactant-free prepared latexes at various stirrer speeds; recipe cf. Figs. 1–3

Monomer/stirrer speed (rpm)	X_{latex} (%)	D_{i} (nm)
MMA/300	89.5	585.8
MMA/600	93.9	573.5
MMA/1200	92.4	395.0
STY/300	75.2	637.0
STY/600	91.8	1253.0
STY/1200	48.1	271.0
TBS/300	0.6	2015.0
TBS/600	2.2	1782.0
TBS/1200	2.0	729.0
LMA/300	17.3	607.8
LMA/600	1.9	164.4
LMA/1200	7.5	236.5

The meaningful evaluation of the latex conversion data requires that the overall polymerization conversion (X, including the amount of coagulum) is comparable. This was the case for the polymerizations considered in Table 1, where X was in any case atleast above 95% as estimated from the amount of coagulum and the solids content of the latex. So, the difference between X_{latex} and 100 is a direct measure of coagulum relative to the amount of monomer. In the cases were low X_{latex} values prove colloidal instability of the system the evaluation of the average size of the final latex particles regarding a mechanistic interpretation requires very likely the consideration of coalescence or coagulation processes.

A closer look at the data in Table 1 reveals that the influence of the stirrer speed on the latex conversion is obviously less pronounced than that of the hydrophilicity of the monomers. For the more hydrophilic MMA and STY X_{latex} is much higher than for the more hydrophobic TBS and LMA. Regarding the average particle size the situation is not so clear as the reason for a small particle size—which is usually a measure for high colloidal stability—can also be a low (latex) conversion. But it is interesting to note that the evaluation of both X_{latex} and D_{i} for TBS and LMA reverses the order regarding hydrophilicity found for MMA and STY.

Another possibility to evaluate heterophase polymerization is the consideration of the efficiency (E), which is defined as interfacial area with respect to mass of stabilizing agent, which in the case of surfactant-free polymerizations is the initiator. The efficiency is a good measure to evaluate heterophase polymerization as it takes account of recipe parameters as well as particle size (colloidal parameter) and monomer conversion (polymerization parameter).

These data put together in Fig. 4 confirm the strong influence of both the stirrer speed and the hydrophilicity of the monomers on the results of stabilizer-free heterophase polymerization. The influence of the stirrer speed is obviously not unambiguously and reflects the two general possibilities, e.g. either increasing or decreasing efficiency. Generally, the stirrer speed affects the colloidal stability, the mixing of both phases, the heat transfer, and the viscosity as discussed in Ref. [21]. Increasing mixing with higher stirrer

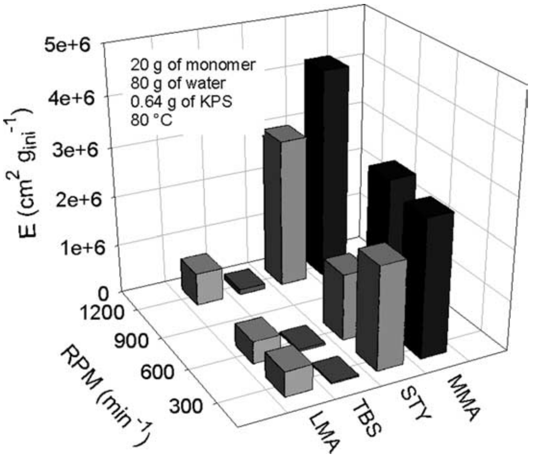


Fig. 4. Efficiencies for e-free polymerizations of MMA, STY, TBS, and LMA in dependence on the stirrer speed.

speed can cause increasing efficiency by means of the smaller drops sizes as discussed above in context with Figs. 1 and 2. Decreasing efficiency indicates shear instabilities of the colloidal system. Interestingly, the efficiencies for the styrene and LMA polymerizations are minimum for the intermediate stirrer speed but maximum for all monomers at the highest stirrer speed. This once more indicates the importance of mixing for surfactant-free emulsion polymerizations.

The efficiencies are at all stirrer speeds lower for the less hydrophobic TBS compared with LMA. These results might be interpreted that at such low level of water solubility as for TBS and LMA the behavior is governed by other molecular properties such as polarity or dipole moments. In this sense the polar ester group in LMA as well as the unique properties of water might be of special importance. But this is speculation at the moment and verification requires specific investigations, which are beyond the scope of this contribution.

In order to improve the latex yield especially for the hydrophobic monomers sets of experiments were carried out in the presence of anionic surfactants: SDS and DSNSG. The experimental data including for the sake of completeness the e-free runs are detailed in Figs. 5 and 6 by means of efficiencies and can be summarized as follows.

The lowest efficiencies are observed for e-free polymerizations. Among these polymerizations the combination KPS/STY is by far the most efficient one due to electrostatic stabilization by sulfate end groups. In the case of PEGA200 the PEG chain length is much too short to impart steric stability to the particles. Contrary, for PEGA4000 the PEG chain length is sufficient and it leads for any monomer to the highest latex yields with 89.4, 99, 99, and 37.5% for MMA, STY, TBS, and LMA, respectively. Moreover, in this case the average particles sizes decrease with decreasing water solubility of the monomers from 5155 nm for MMA, over 320 and 213 nm for STY and TBS, respectively, to 133 nm for LMA.

Employing stabilizers increases the efficiencies considerably thereby being strongly dependent on the particular combination monomer/stabilizer/initiator. For all monomers PEGA4000 leads for both stabilizers to the highest efficiencies followed by PEGA200 and finally KPS. This result might be explained either by an influence of the increased ionic strength for the polymerization with KPS or by synergy between the PEG chains and surfactants as it was discussed recently [22]. The efficiency for KPS and either surfactant tested is the highest for STY as monomer followed closely by MMA. The more hydrophobic monomers TBS and LMA cause much lower efficiencies. The efficiencies obtained for SDS as stabilizer (cf. Fig. 5) follow for all initiators and monomers except the very hydrophobic LMA the well known effect that the stabilizer adsorption is higher for less polar surfaces [23]. Among all monomers investigated STY is the one, where the efficiency changes only little with the different initiator–emulsifier combinations. Surprisingly, the more hydrophilic MMA is more sensitive against changes in the initiator–emulsifier system. In contrast the efficiency for LMA strongly depends on the initiator–emulsifier combination, whereas that for the more water-soluble TBS seems to be less sensitive. Again, these results point to a special role of the ester bond in the comparison of both hydrophobic monomers TBS and LMA.

Considering all experimental results the following dependencies are worth to mention. The average particle size is the smallest in latexes prepared with PEGA200 for all monomers and both surfactants investigated. The latex conversion, especially for the hydrophobic monomers, strongly depends on the particular recipe. For SDS as surfactant LMA as monomer leads comparing all initiators and monomers to the lowest latex conversion. For the more hydrophilic monomers (MMA, STY, TBS) X_{latex} is in any case above 90%, whereas for LMA it is 17.2, 18.4, and 56.6% for KPS, PEGA200, and PEGA4000, respectively. If SDS is replaced by DSNSG the same general trend is observed with the exception that the combination TBS/PEGA200/DSNSG ends with a powdery solid, where the water is included in the polymer acting as 'continuous phase' (determination of the solids content gives the theoretical value). The latex conversions for the LMA polymerizations with KPS, PEGA200, and PEGA4000 are 17.7, 15.6, and 99.0%, respectively. The latter value is the highest X_{latex} for LMA obtained in the investigations and indicates that the combination DSNSG/PEGA4000 is especially suited to get also for hydrophobic monomers in 'normal' ab initio heterophase polymerizations that is, without applying special emulsification techniques, acceptable results (cf. in Fig. 6 the efficiency graph for LMA).

The experimental results regarding the molecular weight of the various polymers present in the latex particles reveal, beside a strong influence of the hydrophilicity of the monomers, the importance of the initiator stabilizer combination.

The overview in Fig. 7 shows that MMA leads in almost

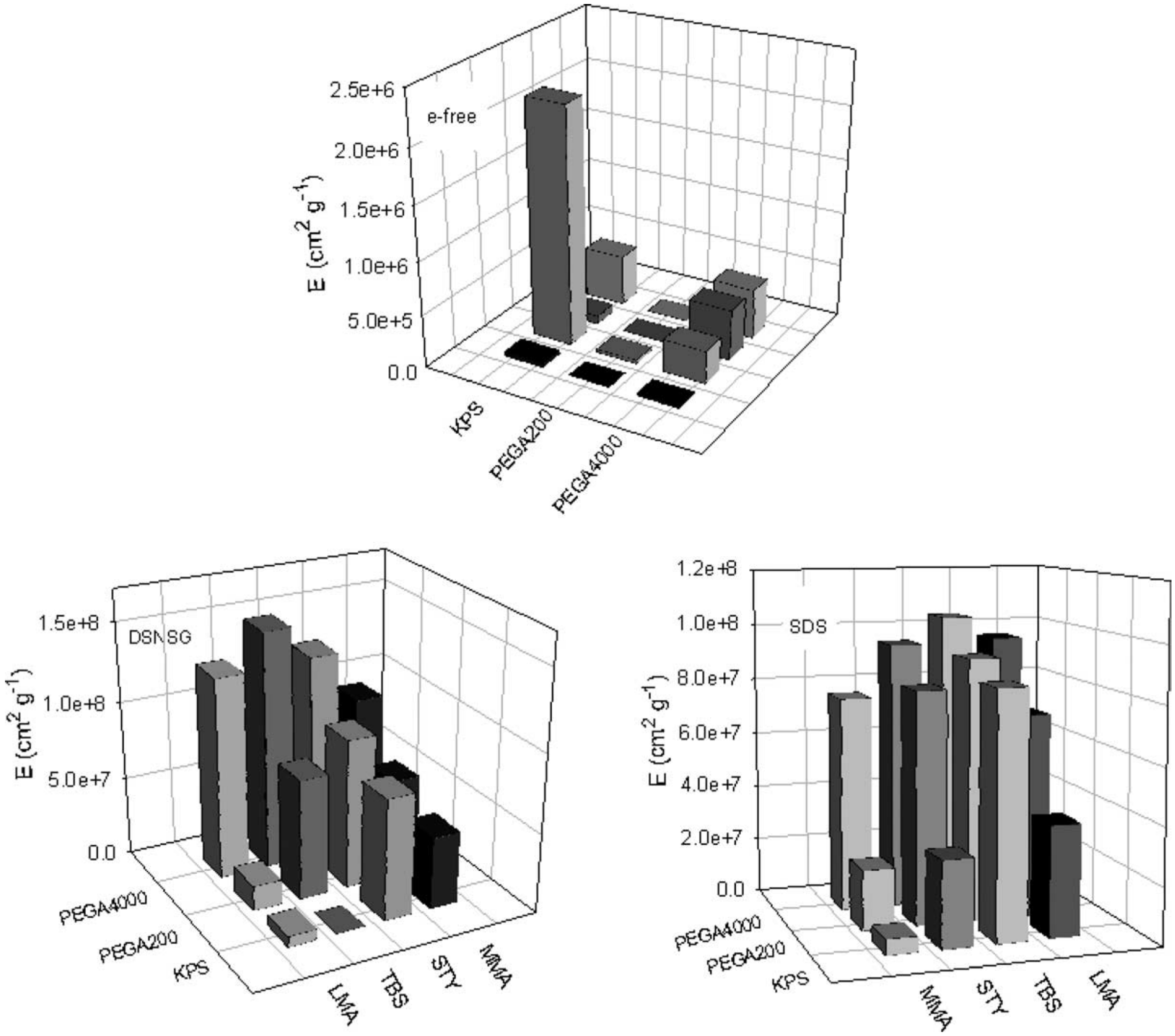


Fig. 5. Efficiency in aqueous heterophase polymerizations for various combinations of monomers, initiators, and stabilizers grouped by stabilizer; polymerization conditions: 40 g of water, 10 g of monomer, 0.1 g of stabilizer, 30 mM initiator, 80 °C, 300 rpm.

all cases studied to the highest molecular weights, except for the combinations PEGA200/e-free and KPS/DSNSG, where STY gives the polymers with highest molecular weights.

It is interestingly to mention that for the hydrophobic monomers in the cases, where the latex yield is extremely low also the molecular weight of the polymers in the particles is low. This effect is extremely pronounced for the polymerization of LMA with KPS for all stabilizers with M_w-values in the order of 5×10^3 g mol^{-1}. However with PEGA200 in the presence of surfactants and comparable latex yields the M_w-values are two orders of magnitude higher. These statements hold despite the fact that the molecular weights were calculated based on polystyrene calibration curves. However, the detailed discussion of the molecular weight data is very complex and is beyond the aim of this experimental study. On the one hand it is necessary to consider the particular influence of all recipe components on chain transfer and on the other hand on the colloidal properties such as the average particle size as it determines the radical and monomer concentration at the main reaction loci, which are the monomer swollen particles.

The data presented so far revealed that it is not an easy undertaking to get high latex yields with only very hydrophobic monomers such as LMA. One way to solve this problem was found in the use of cyclodextrin as phase transfer agent [24–27]. Another possibility is the use of special surfactants such as DSNSG in combination with PEGA-initiators with longer poly(ethylene glycol) chains thus changing the hydrophilic–hydrophobic balance of the polymer molecules formed.

All three the latex yields, the average particle diameters, and the efficiencies increase with increasing PEG chain length of the PEGA-initiators as the data in Fig. 8 confirm.

These results show the astonishing effect that the stability is dominated by the kind of initiating radical even in the presence of an effective stabilizer such as DSNSG. This is obviously a consequence of the extremely hydrophobic LMA as in the case of STY only minor differences in latex

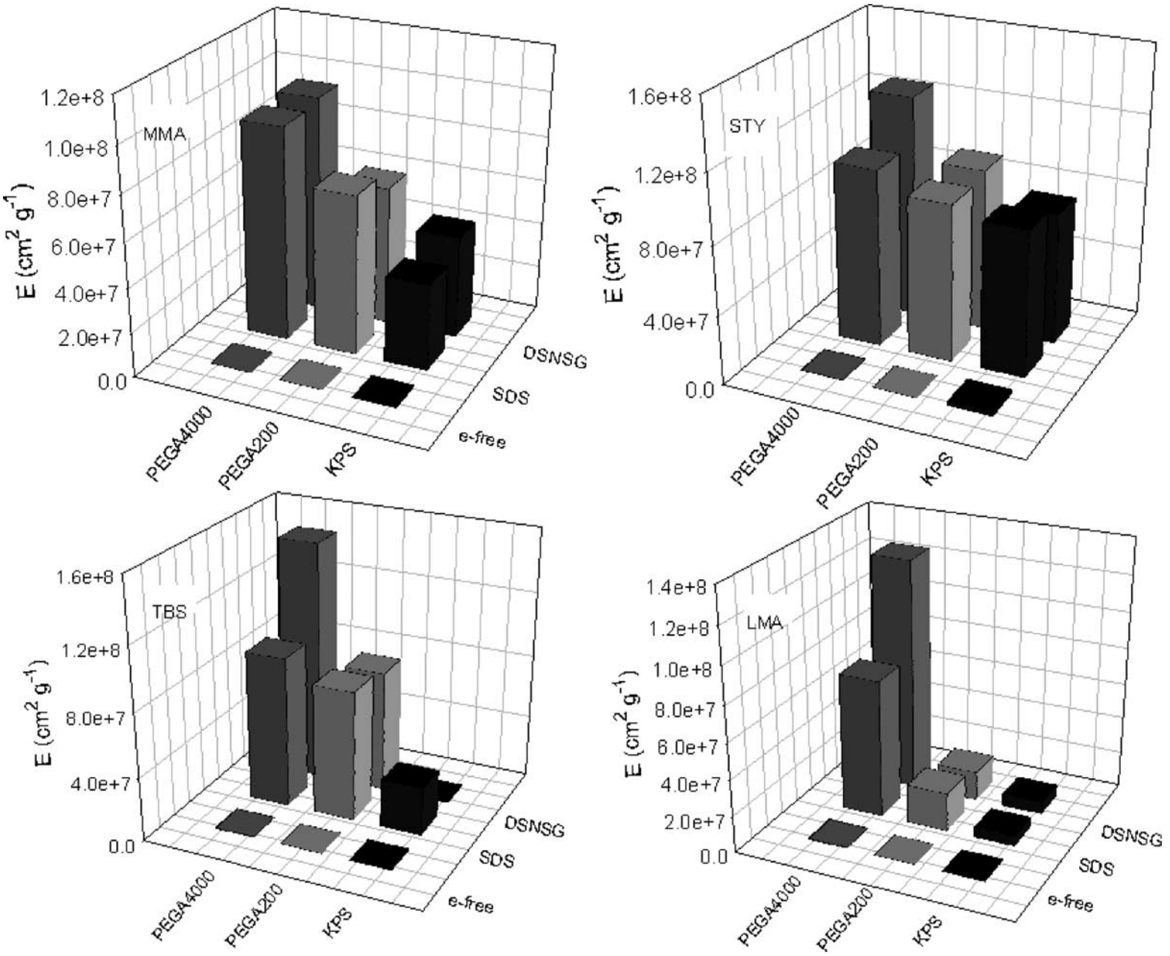


Fig. 6. Efficiency in aqueous heterophase polymerizations for various combinations of monomers, initiators, and stabilizers grouped by monomer; polymerization conditions: 40 g of water, 10 g of monomer, 0.1 g of stabilizer, 30 mM initiator, 80 °C, 300 rpm.

properties and kinetics between KPS and hydrophobic initiators such as BPO and AIBN have been found [28,29]. It is not surprising that in the case of LMA the stabilization is better the higher the PEG molecular weight as longer PEG chains influence the hydrophilic–hydrophobic balance of both the individual polymer chains and the particles much stronger. It is important for the evaluation of these results that the PEGA initiators lead to the formation of amphiphilic block copolymers with increasing hydrophilic block chain length from PEGA200 to PEGA4000. Another explanation might be that specific interactions between the PEG chains and the LMA molecules influence the LMA partition between the droplets and the aqueous phase. Such interaction should be favored the longer the PEG chain.

A closer look at the results obtained with various initiator/stabilizer combinations as detailed in Table 2 clearly shows the synergy between PEGA4000 and DSNSG for LMA as all other combinations lead to much lower latex conversions and efficiencies.

Also the morphology of the coagulum strongly depends on the particular initiator/stabilizer combination. Whereas KPS/DSNSG leads to a whole piece of sticky coagulum PEGA initiators cause the formation of rice-like shaped grains sticking together. The dimensions of the grains decrease as the PEG chain length increases thus reflecting better stability and/or increasing tendency to phase separation of both blocks.

A third possibility to increase the latex yield for hydrophobic monomers is the polymerization inside preformed stable emulsion droplets (so-called miniemulsion

Table 2
Latex yield, efficiency, and average particle size for LMA heterophase polymerization with different initiator–stabilizer combinations

Initiator/stabilizer	D_i (nm)	E (cm^2 g^{-1})	X_{latex} (%)
PEGA200/DSNSG	69.0	1.6×10^7	15.6
PEGA200/SDS	58.5	2.1×10^7	18.4
PEGA4000/DSNSG	109.8	1.3×10^8	99.0
PEGA4000/SDS	134.0	7.6×10^7	56.6
KPS/DSNSG	159.8	$6.5.\times10^6$	17.7
KPS/SDS	187.6	5.4×10^6	17.2

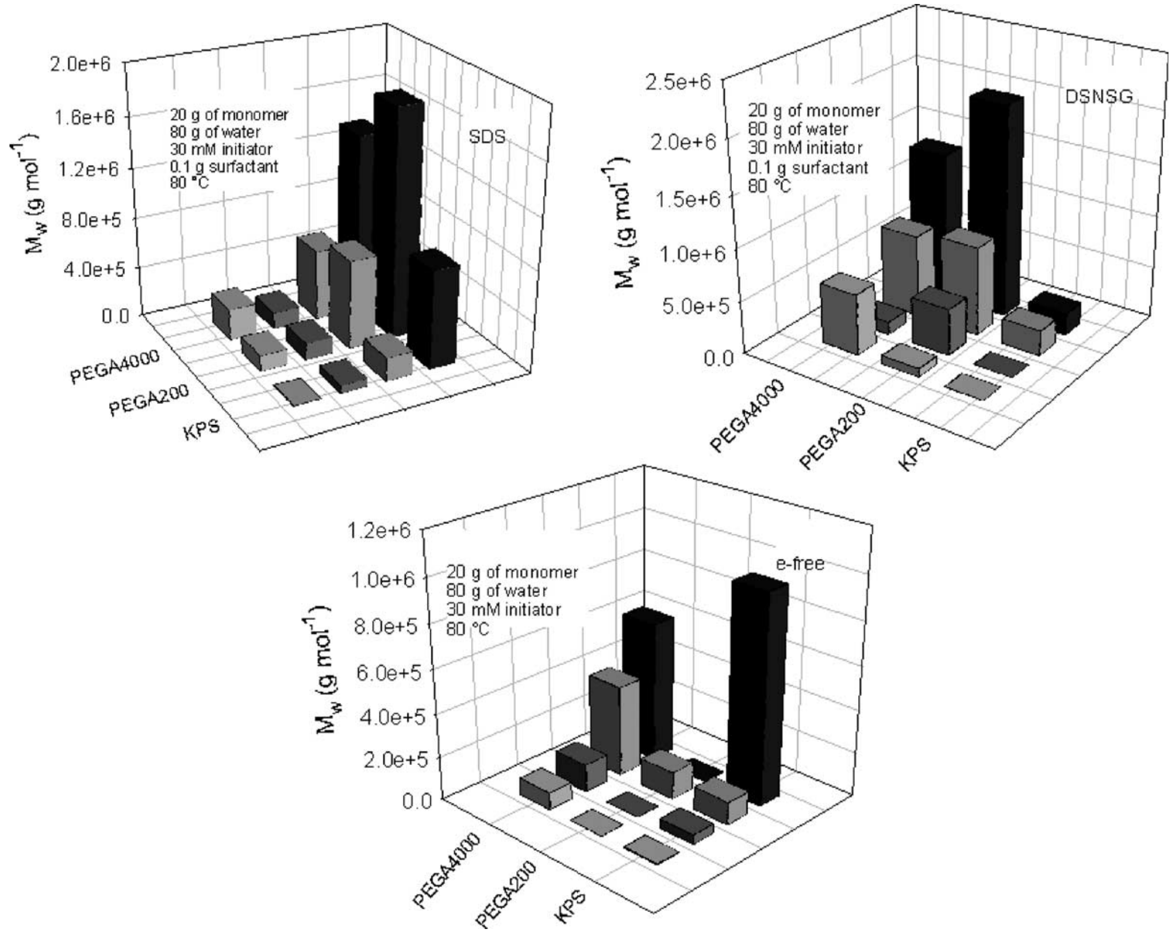


Fig. 7. Weight average molecular weights (M_w) of the polymers present in latex particles obtained with various combinations of monomers, initiators, and stabilizers grouped by stabilizer.

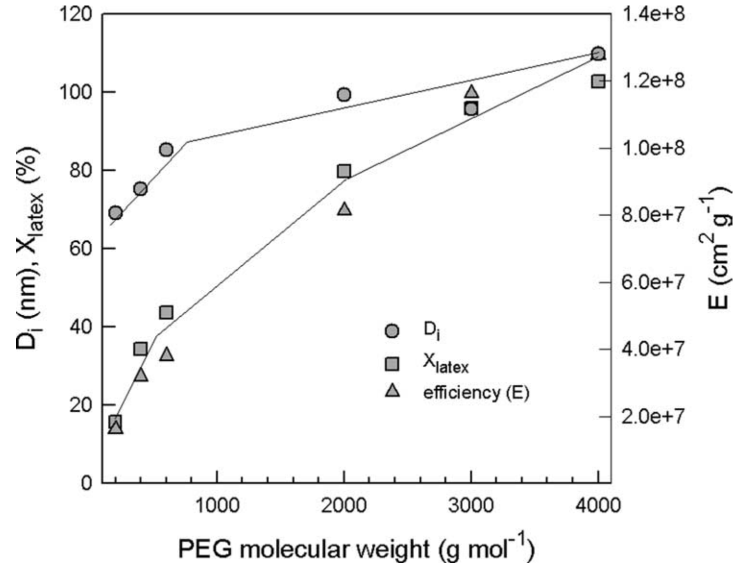


Fig. 8. Average particle size, latex conversion, and efficiency for emulsion polymerizations of LMA with DSNSG as stabilizer and PEGA initiators of various PEG chain lengths; the lines are just for guiding the eyes.

polymerization). The low solubility of these monomers in water favors the formation of droplets by comminution techniques (homogenizers or ultrasonication nozzles), which under optimum conditions are stable against degradation by diffusion processes over time scales longer than the polymerization time [30,31]. For these polymerizations the average drop sizes (measured before polymerization) and the average particles sizes (after polymerization) differ. This clearly means that a 1:1-copy of these particular miniemulsion droplets by polymerization was not achieved. For the LMA polymerizations, the ratio between drop and particle size depends on the nature of the initiator. For PEGA200 the drop size is lower than the particle size, whereas for KPS the reverse is generally observed [32]. Regardless the fact that 100% droplet nucleation is not achieved the data put together in Fig. 9 show exemplary for DSNSG as surfactant the benefit of this special type of heterophase polymerization for very hydrophobic monomers comparing results for STY, TBS, and LMA with KPS or PEGA200 as initiator. Considering average particle size, efficiency and latex yield the following conclusion are remarkable. The slight differences regarding the surfactant concentration relative to the mass of monomer and the polymerization temperature between both recipes are not sufficiently to affect the conclusions.

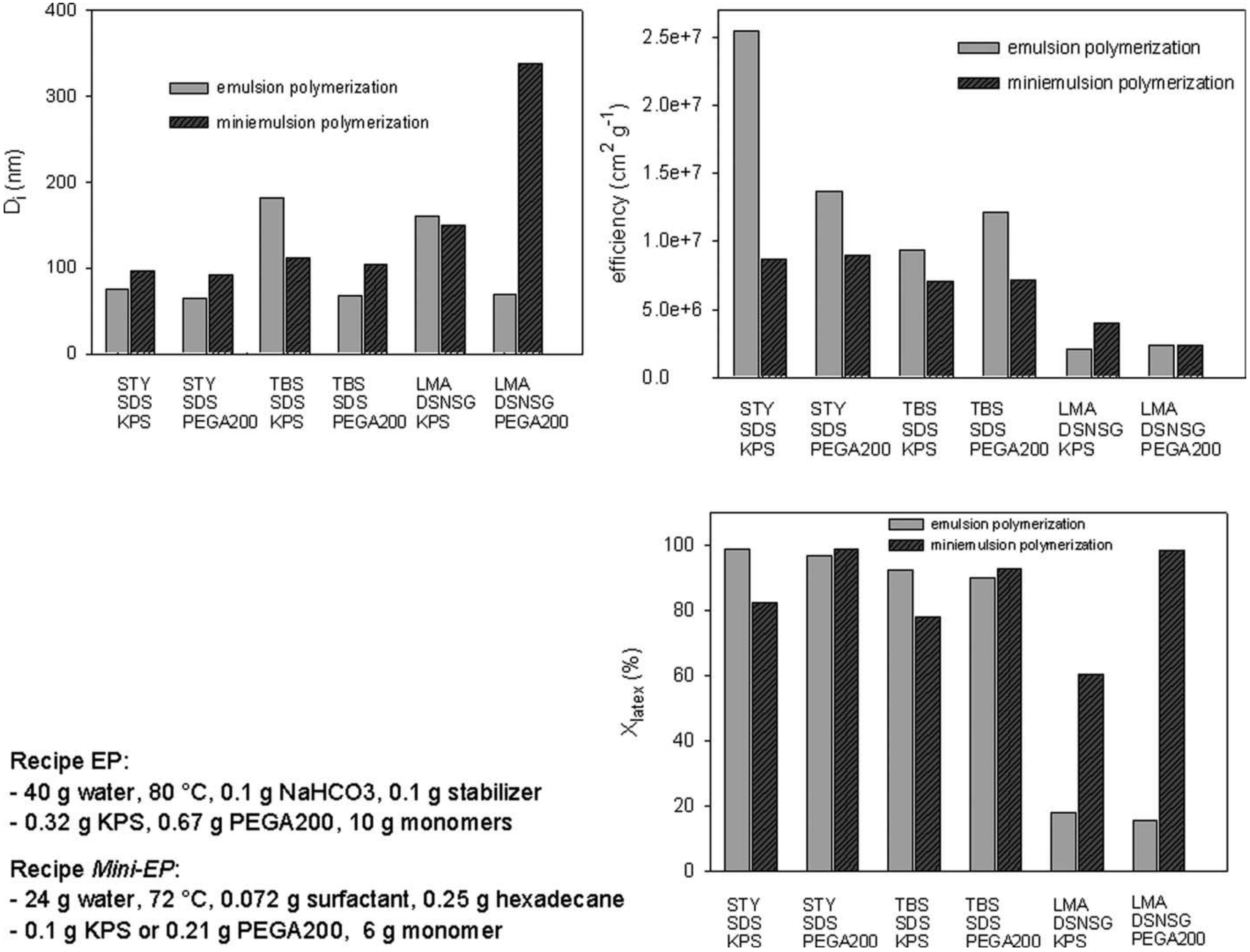
The average particle size of the latexes prepared via miniemulsion polymerization shows a clear tendency to increase with increasing hydrophobicity of the monomer. This effect is especially pronounced for the less hydrophilic PEGA200 as initiator, which has a water-solubility of about only 2.6 g l^{-1} [33]. Contrary, for the emulsion polymerization latexes prepared with PEGA200 the average particle size is almost unaffected by the hydrophobicity of the monomers. For both heterophase polymerization systems and either initiator the efficiency decreases with increasing hydrophobicity. The latex yield for LMA depends in the case of miniemulsion polymerization strongly on the kind of initiator as X_{latex} for KPS is much smaller than for PEGA200.

The requests at initiator/stabilizer combinations regarding the production of stable latexes as considered so far for only slightly hydrophilic and hydrophobic monomers change completely if polymer dispersions from highly hydrophilic monomers such as HEMA should be prepared by aqueous heterophase polymerization. Although this monomer is unlimited soluble in water the polymer is not but only swellable [34]. The Flory–Huggins interaction coefficient for poly-HEMA–water and poly-HEMA–HEMA is about 0.8 and 0.57, respectively. Both values increase with increasing polymer volume fraction and thus, phase separation takes place during polymerization. Poly-HEMA is in the dry state a hard and brittle polymer with a glass transition temperature of about 86 °C [13] but soft and flexible in the swollen state. It is capable of swelling in water and aqueous electrolyte solutions to a degree of about 50% by weight but in sodium hydroxide solution up to 150% [35].

The preparation of poly-HEMA particles in the submicron size range by aqueous heterophase polymerization is not an easy undertaking. Only one research group described recently the preparation of poly-HEMA particles in a size range of about 100 nm using SDS and AIBN [36,37]. According to these results the experimental conditions with regard to initiator and emulsifier as well as stirring speed are very crucial. For instance, latex formation was not observed for KPS as initiator, or poly(vinyl alcohol) as sole stabilizer, or high solids content, or at stirrer speeds clearly above 100 rpm [36]. A recipe published in Ref. [37] with a medium SDS concentration was the starting point for our investigations focusing on the influence of various types of initiators and the influence of the hydrophobic–hydrophilic balance of alkyl sulfate stabilizers and surface active inisurfs.

Table 3 summarizes experimental data obtained with different initiators. Comparable with the above results obtained for the hydrophobic LMA (cf. Fig. 7) also for the hydrophilic HEMA the polymerization results strongly depend on the hydrophilicity or hydrophobicity of the initiator, which is not the case for STY [28,29]. The water-soluble KPS leads to almost complete coagulation (latex yield about 8%), whereas the hydrophobic AIBN and BPO cause high latex yields, much smaller particles, and higher efficiencies. Concerning their hydrophobic–hydrophilic properties PEGA initiators are situated somewhere in the middle between the hydrophilic and hydrophobic initiators investigated so far. PEG is soluble in water but also in many organic solvents. It possesses a lower critical solution temperature, which is inversely proportional to the molecular weight, and becomes more and more hydrophobic with increasing temperature [38]. These properties of PEG are clearly reflected in the polymerization results as PEGA 200 resulted in lower latex yield and efficiency than PEGA4000. Moreover, surfactant-free polymerizations resulted for both PEGA's in zero latex yields that is, complete coagulation occurred.

The strong influence of the hydrophobicity of the primary radicals led to the conclusion that also the hydrophilic–hydrophobic balance of the stabilizer might strongly influence the polymerization. The hydrophilic–hydrophobic balance of the initiator emulsifier system (IES) was varied by employing either sodium alkyl sulfates of different alkyl chain length (6, 8, 10, 12, 14, 16, 18) at given hydrophobic initiator (AIBN) or surface-active initiators prepared with α-olefins of different alkyl chain length (5, 8, 10, 14, 16). The results regarding efficiency and latex yield are put together in Fig. 10 and reveal indeed a strong influence of the alkyl chain length of the surfactant and the insurf. The interesting result is that in dependence on the alkyl chain length both curves for the alkyl sulfate surfactants go through a maximum, whereas they reach a constant value for the inisurfs with increasing carbon



Recipe EP:
- 40 g water, 80 °C, 0.1 g NaHCO3, 0.1 g stabilizer
- 0.32 g KPS, 0.67 g PEGA200, 10 g monomers

Recipe *Mini-EP*:
- 24 g water, 72 °C, 0.072 g surfactant, 0.25 g hexadecane
- 0.1 g KPS or 0.21 g PEGA200, 6 g monomer

Fig. 9. Comparison of average particle size, latex conversion, and efficiency for emulsion polymerizations of STY, TBS, and LMA with DSNSG as stabilizer and KPS or PEGA200 as initiator.

Table 3
Influence of the initiator hydrophobicity on aqueous heterophase polymerization of HEMA (recipe: 185 g of water, 15 g of HEMA, 0.35 g SDS; 0.2 g of initiator (4 g of PEGA4000), 60 °C, 100 rpm)

Initiator	FG (%)	X_{latex} (%)	D_{I} (nm)	E (cm^2 g^{-1})
AIBN	7.53	97.0	88.8	$2.26 \cdot 10^7$
BPO	7.86	100.0	94.3	$2.22 \cdot 10^7$
KPS	0.87	8.0	248.2	$8.70 \cdot 10^5$
PEGA200	5.47	70.0	131.0	$1.09 \cdot 10^7$
PEGA4000	9.91	100	230.0	$1.18 \cdot 10^7$

number. It is interesting to note that an absolutely comparable behavior of the inisurfs was also observed for monomers with increasing hydrophobicity such as methyl methacrylate and butyl methacrylate [39] as well as styrene [40,41].

The common feature in both cases considered in Fig. 10 is that aggregation of oligomers takes place due to the interaction of initiator end groups. As aggregation starts when a proper hydrophilic–hydrophobic balance of the oligomers is reached the HEMA chain length at precipitation strongly depends on the hydrophobicity of the initiating radicals. This controlled or by the initiator end groups induced aggregation is obviously a necessary prerequisite for the formation of well-defined, nanosized poly-HEMA particles. If the aggregation is caused alone by the increasing hydrophobicity of the growing poly-HEMA chains the resulting particles do not contain the regions of much higher hydrophobicity of the initiator residuals. The experimental results with the different initiators either the common types such as KPS, AIBN, and BPO at given SDS concentration or the inisurfs, where undecomposed molecules act simply as surfactant molecules, lead to the conclusion that the presence of hydrophobic domains inside the particles is absolutely necessary for surfactant adsorption causing stability of the nanosized particles against coagulation.

Whether or not surfactant molecules with a given alkyl chain length will adsorb and prevent coagulation depends on the energy that the systems can gain as different phases compete for the surfactant molecules. The continuous phase, where the surfactants are dissolved, the interface, where the surfactants are adsorbed, and the micellar phase, where the surfactants are self-assembled. Which of these states will be favored depends on the hydrophobic–hydrophilic balance of the particular surfactant molecules. For the aqueous phase polymerization of HEMA with AIBN as initiator and sodium alkyl sulfate surfactants with carbon numbers below 10 the surfactants favor the continuous phase, whereas for carbon numbers above 14 self-assembly of the surfactant molecules is dominating. The optimum alkyl chain lengths regarding stabilization of the poly-HEMA water interface are obviously 12 and 14 meaning that these alkyl sulfates prefer to be adsorbed.

For the inisurfs the situation is slightly different as they affect both the nucleation and the stabilization of the particles. Changing the alkyl chain length causes a change of the hydrophobicity of the poly-HEMA end group as well and thus influencing directly the primary aggregation process. An increase in the carbon number should lead to higher efficiency as verified by the experimental results. Moreover, each new polymer chain contributes to stability

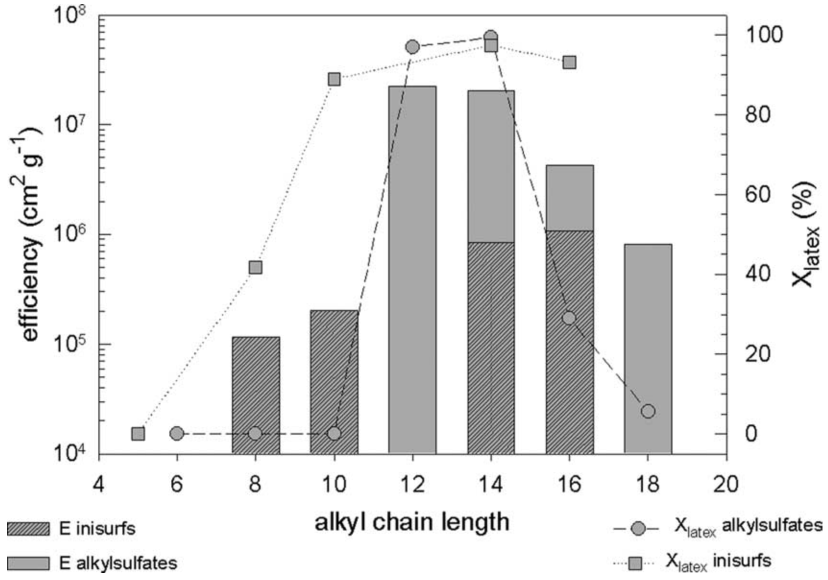


Fig. 10. Efficiency and latex conversion for HEMA polymerization with different initiator–stabilizer systems (60 °C).

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 initiator–emulsifier combination as the hydrophobic domain and the adsorbing moiety are chemically identical and have also the same chain length.

4. Conclusions and summary

The particular hydrophobic–hydrophilic situation for a given aqueous heterophase polymerization determines the final results of the process. For ab initio batch polymerizations the solubility of the monomer in the continuous phase is on the one hand of paramount importance regarding the choice of a proper initiator/stabilizer combination in order to get optimum polymerization results. On the other hand it also determines the effort that must be used for the manufacture of the starting emulsion especially for extremely hydrophobic monomers and common initiator/-stabilizer combinations.

Polymerization conditions and recipes, which are optimum for styrene, have to be modified regarding recipe components and possibly also regarding the emulsification procedure to get for much more hydrophilic or hydrophobic monomers equally good results. It turned out that for comparing evaluation the average particle size (as indirect quantitative measure of the dispersity), the latex conversion (as direct measure to what extent the starting emulsion was transferred into the final colloidal polymer dispersion), and the interface between polymer and the continuous phase formed per unit mass of stabilizer (efficiency) are very useful. All three values allow an almost objective and quantitative characterization of a given heterophase polymerization.

Moreover, the experimental results clearly prove the importance of the properties of the initiating radicals in ab initio heterophase polymerizations especially for monomers with either lower or larger hydrophobicity than styrene. In order to get high latex yields, small particles sizes, and high efficiencies more hydrophilic monomers such as 2-hydroxyethyl methacrylate require hydrophobic initiating radicals, whereas in the case of more hydrophobic monomers such as lauryl methacrylate hydrophilic polymeric radicals are necessary.

In final conclusion, hydrophobicity and hydrophilicity of any of the recipe components in aqueous heterophase polymerizations are important features as their interplay is crucial for the course of the reaction. Moreover, this way of considering aqueous heterophase polymerizations needs some remarks regarding the role of water in the whole process of creation of polymer dispersions. If the knowledge of the polymerization mechanism is still today, more than 90 years after the first synthetic heterophase polymerization [42], insufficient in many important aspects (cf. [14,15,42]) then, it is beyond question that concerning the role of water the situation is really blameful and is even exaggerated to say that there is a beginning of its understanding. Important questions, which should be addressed in future research activities, include the solution state of monomers as well as the state and the role of dissolved gases. First results as described in Ref. [43] regarding the initial state of ab initio aqueous heterophase polymerizations show indeed that these are important topics towards a better understanding.

References

[1] Tanford C. The hydrophobic effect: formation of micelles and biological membranes. New York: Wiley; 1973 [pp. 1–3].

[2] van Es JJGS, Geurts JM, Verstegen JM, German AL. Some trends in the preparation and use of reactive latexes. In: Asua JM, editor. Polymeric dispersions: principles and applications. Dordrecht: Kluwer Academic Publishers; 1997. p. 451–62.

[3] Vanderhoff JW. Chem Eng Sci 1993;48(2):203–17.

[4] Yalkowsky SH, Banerjee S. Aqueous solubility—methods of estimation for organic compounds. New York: Marcel Dekker; 1992. p. 41–127.

[5] Nedez C, Ray J-L. Langmuir 1999;15(18):5932–6.

[6] Czichocki G, Vollhardt D, Seibt H. Tens Deterg 1981;18(6):320–7.

[7] Sedlak M, Tauer K. Synlett 2004;(2):299–300.

[8] Tauer K, Antonietti M, Rosengarten L, Müller H. Macromol Chem Phys 1998;199:897–908.

[9] Landau RN. Thermochim Acta 1996;289:101–26.

[10] de la Rosa LV, Sudol ED, El-Aasser MS, Klein A. J Polym Sci A: Polym Chem 1996;34:461–73.

[11] Tauer K, Müller H, Schellenberg C, Rosengarten L. Colloid Surf A: Physicochem Eng Aspects 1999;153:143–51.

[12] Yildiz U, Landfester K, Antonietti M. Macromol Chem Phys 2003; 404(16):1966–70.

[13] Shen MC, Strong JD, Matusik FJ. J Macromol Sci Phys 1967;B1(1): 15–27.

[14] Gilbert RG. Emulsion polymerization—a mechanistic approach. London: Academic Press; 1995.

[15] El-Aasser MS, Sudol ED. Features of emulsion polymerization. In: Lovell PA, El-Aasser MS, editors. Emulsion polymerization and emulsion polymers. Chichester: Wiley; 1997. p. 37–58.

[16] Okamura S, Motoyama T. J Polym Sci 1962;58:221–7.

[17] Tauer K. Surface chemistry in the polymerization of emulsion. In: Holmberg K, editor. Handbook of applied colloid and surface chemistry. New York: Wiley; 2001. p. 175–200.

[18] Defay R, Prigogine I. Surface tension and adsorption. London: Longmans, Green and Co., Ltd; 1966 [pp. 259–284].

[19] Ugelstad J, El-Aasser MS, Vanderhoff J. J Polym Sci C: Polym Lett 1973;11(8):503–13.

[20] Hergeth W-D, Bloß P, Biedenweg F, Abendroth P, Schmutzler K, Wartewig S. Makromol Chem 1990;191(12):2949–55.

[21] Zubitur M, Asua JM. Polymer 2001;42(14):5979–85.

[22] Tauer K, Müller H. Colloid Polym Sci 2003;281:52–65.

[23] Vijayendran BR. J Appl Polym Sci 1979;23:733–42.

[24] Rimmer S, Tattersall P. Polymer 1999;40(20):5729–31.

[25] Rimmer S. Macromol Symp 2000;150:149–54.

[26] Leyrer RJ, Mächtle W. Macromol Chem Phys 2000;201(12):1235–43.

[27] Lau W. Macromol Symp 2002;182:283–9.

[28] Breitenbach JW, Edelhauser H. Makromol Chem 1961;44–46: 196–211.

[29] Asua JM, Rodriguez VS, Sudol ED, Elaasser MS. J Polym Sci A: Polym Chem 1989;27(11):3569–87.

[30] Kabalnov AS, Pertzov AV, Shchukin ED. Colloid Surf 1987;24:19–32.
[31] Tauer K. Polymer 2005 [this issue].
[32] Yildiz U, Landfester K, Antonietti M. Macromol Chem Phys 2003;204(16):1966–70.
[33] Müller H. Polymere stabilisatoren in der emulsionspolymerisation-hairy particles. PhD Thesis. Teltow: University of Potsdam; 1997, pp. 31–41.
[34] Dusek K, Sedlacek B. Eur Polym J 1971;7:1275–85.
[35] Rosenberg M, Bartl P, Lesko J. J Ultrastr Res 1960;4:298–303.
[36] Chu H-H, Fu D-C. Macromol Rapid Commun 1998;19:107–10.
[37] Chu H-H, Ou E-D. Polym Bull 2000;44:337–44.
[38] Bailey Jr FE, Koleslke JV. Poly(ethylene oxide). New York: Academic Press; 1976 [pp. 29–86].
[39] Ali AMI, Tauer K, Sedlak M. Polymer 2005 [this issue].
[40] Aslamazova T, Tauer K. Adv Colloid Interface Sci 2003;104:273–83.
[41] Aslamazova T, Tauer K. Colloid Surf Physicochem Eng Aspects 2004;239(1–3):3–10.
[42] Tauer K. Heterophase polymerization. In: Kroschwitz JI, editor. Encyclopedia of polymer science and technology. New York: Wiley-Interscience; 2003.
[43] Kozempel S, Tauer K, Rother G. Polymer 2005 [this issue].