Interfacial Energy Promotes Radical Heterophase Polymerization

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ABSTRACT: Experimental evidence is presented that during the conditions of aqueous heterophase polymerization radical generation and subsequent polymerization are induced by the interfacial energy. A comprehensive study of the emulsion polymerization of styrene at 25 °C with various types of emulsifiers and with different nonredox initiators such as potassium peroxodisulfate, 2,2′-azoisobutyronitrile, dibenzoyl peroxide, and poly(ethylene glycol)-azo-initiator reveals that the particular initiator−stabilizer combination has a strong influence on the achievable final conversion and the latex properties. The deceleration of the polymerization due to the low temperature allowed the recognition of basic differences in the behavior of monomer- and water-soluble initiators, especially at low conversions during the prenucleation period.

Introduction

Radical polymerizations start with a sequence of two reactions during the initiation stage.[1] The first is the generation of free radicals ($R^\bullet$) by any reaction from a multiplicity of possibilities such as homolytic cleavage of thermolabile compounds, redox couples, or thermal self-reaction of monomers. The second step is the addition of these radicals to single monomer molecules to produce the species $R-M_1^\bullet$ starting the chain growth. Thus, high initiation rate requires fast production of $R^\bullet$ and high concentration of monomer in spatial proximity. The overall rate of subsequent polymerization is mainly determined by the concentration of growing radicals, the monomer concentration, and the propagation rate constant. This scenario is more complicated in heterophase polymerization due to the existence of at least two reaction loci: one in the continuous phase and the other in the dispersed phase. For aqueous heterophase polymerization of styrene, the disperse phase, that is, the monomer-swollen particles, is the main loci of monomer conversion.[2,3] If water-soluble initiators such as peroxodisulfates and redox couples are employed, initiation takes place in the continuous phase. Also, for oil-soluble initiators there is evidence that despite minor differences the overall polymerization kinetics is mainly determined by aqueous phase initiation.[4−8] Despite all the similarities between oil- and water-soluble initiators regarding the overall kinetics, differences in the copolymer composition for comonomers with different polarities have been observed.[9] Furthermore, the kinetics of organic peroxides and hydroperoxides in heterophase polymerizations depends strongly on the polarity of the initiator molecules.[10] These authors observed that the ratio between the rate of initiation in emulsion polymerization with surfactant concentrations above the critical micelle concentration and bulk polymerization of styrene at 60 °C is for the hydroperoxides (highest for *sec*-butyl hydroperoxide) by a factor between 100 and 10^4 larger than 1 but in any case higher than for the symmetrical peroxides (highest is dibutyl peroxide with a factor of about 30). For very hydrophobic peroxides such as dibenzoyl peroxide and dipalmitoyl peroxide the ratio equals 1, meaning that initiation takes place in either polymerization system in the monomer phase. Especially for the hydroperoxides there is an optimum polarity that forces the initiator molecules toward the interface to water where interfacial forces might facilitate the homolytic cleavage. The influence of the polarity or hydrophilicity of oil-soluble initiators has been confirmed as it was found that the importance of water phase kinetics for emulsion polymerization of styrene follows the order 2,2′-azoisobutyronitrile > dibenzoyl peroxide (BPO) > lauroyl peroxide.[11]

Peroxodisulfates, organic azo compounds, peroxides, and hydroperoxides are generally used in the temperature range 50−100 °C to produce $R^\bullet$ by homolytic cleavage. But they can be used also at lower temperatures 0−50 °C as part of redox systems.[12] Moreover, organic peroxides and azo compounds can be synthesized possessing thermolytic decomposition at temperatures clearly below 50 °C, but their practical application to polymerization reactions is restricted due to only short storage times and enhanced safety problems. Exemplary can be mentioned *p*-(1,1-dicyanoethylazo)-benzenesulfonic acid, an asymmetric azo-initiator, which decomposes in a pH range 1−7 according to first-order kinetics.[13] With this initiator the authors report emulsion polymerization of styrene with sodium dodecyl sulfate as surfactant at concentration above the critical micelle concentration at 25 °C and pH = 4.62 where the decomposition rate constant is about 1.4×10^{-6} s^{-1}. Within 500 min conversion of about 60% has been obtained. However, at low temperatures redox systems are clearly favored as they allow a much better control of the initiation rate as the concentration of at least one component can changed by feeding on demand.

Because of their heterogeneous nature, heterophase polymerizations generally require the presence of auxiliary materials most importantly surface-active compounds (stabilizers or surfactants or emulsifiers) to preserve colloidal stability. All the pros and cons of heterophase polymerizations are connected with the compartmentalization of the reaction system or in other words with the existence and the stabilization of the

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interface.[14] There is also experimental evidence that surfactants and/or interfaces influence the rate of initiation and the initiator decomposition in aqueous systems.[15−19] Despite the fact that some caution should be exercised regarding the explanation of experimentally observed faster rates of polymerization with increased initiation rate or initiator decomposition such as done in refs 10, 15, and 16 as already the higher degree of dispersity in dependence on soap concentration can result in faster polymerization rates,[20] there is also clear experimental evidence that the initiator decomposition is accelerated by the presence of surfactants.[17−19] Exemplary, it was experimentally observed[19] that the decomposition rate of potassium peroxodisulfate (KPS) clearly depends on the concentration of hexaethoxyalkylmaleate and -succinate surfactants. Furthermore, the Arrhenius energy of activation decreases with increasing surfactant concentration for all investigated alkyl chain lengths from 9 to 16. Anionic emulsifiers such as sodium dodecyl sulfate (SDS) and hexadecyl sulfate also markedly increase the persulfate decomposition rate.[17] An interesting study was carried out on the influence of a heterogeneous environment on initiator decomposition in aqueous micellar solutions of sodium dodecyl sulfate and cetyltrimethylammonium bromide (CTAB) wherein 2,2′-azoisobutyronitrile (AIBN) was dispersed by ultrasonication.[18] These authors observed a decomposition rate constant at 60 °C of $1 \times 10^{-5}\ \mathrm{s}^{-1}$, which is only slightly higher than that determined in styrene[21] or in styrene/toluene mixtures,[22] thus supporting the experience that the decomposition of azo-initiators is compared with peroxides only little sensitive to solvent effects.[23] Furthermore, the authors were able to show that the charge of the micelles either anionic SDS or cationic CTAB has an effect neither on the decomposition of AIBN nor on the escape of 2-cyano-2-propyl radicals from both the cage and the micelles as proven by the application of different inhibitors.

All these results, obtained in a temperature range between 50 and 100 °C, clearly support the assumption that the initiation reaction of radical heterophase polymerizations is more complex than in homogeneous systems without interfaces. Unfortunately, in this temperature range thermal initiator decomposition takes place to a large extent, and thus, supposed influences of the interfacial forces on radical formation, which should act like temperature, could not be detected clearly and independently. The local environment on micrometer or nanometer length scales as expressed by interfacial forces can influence chemical reactions and physical behavior of substances in contact with interfaces. Of special importance is in this sense the polarity of both the host interfacial layer and the guest molecule as it determines the distribution of guest molecules inside micelles. Polar guest molecules evidently stay in the polar interfacial region, but it has been experimentally found that also nonpolar molecules such as benzene solubilized in various types of micelles prefer to stay close to the interface to water. The driving force for this is that the interfacial tension of benzene against water is lower than that against the hydrocarbon forming the micellar core.[24] The influence of the polar micelle−water interface on radical reactions such radical induced oxidation reactions is known since a long period of time.[25,26]

Considering all the above information, questions arise to what extent interfaces and interfacial forces are really able to influence the kinetics and the course of heterophase polymerizations. If yes, what is the influence of the polarity or the hydrophilicity of the initiator, do oil-soluble and water-soluble initiators behave similarly, is there an influence of the type of surfactant, and what is the role of the polarity of the monomer? To answer at least some of these questions independently of too strong thermal influences, polymerization experiments are required at temperatures as low as possible to see whether interfacial forces can promote initiator decomposition and the formation of polymerizable radicals. The paper reports on results of aqueous ab initio heterophase polymerizations of styrene with different initiator−emulsifier combinations at temperature of 25 °C. The initiators and emulsifiers are KPS, AIBN, BPO, PEGA200 (symmetrical poly(ethylene glycol)-azo-initiator with poly(ethylene glycol) chains of 200 g mol^{-1}) and SDS, CTAB, IGEPAL CO880 (ethoxylated nonylphenol with a molecular weight of the poly(ethylene glycol) of about 880 g mol^{-1}), TEGO LA-S 687 (symmetrical triblock copolymer with poly(dimethylsiloxane) middle block (about 20 siloxane units) with to side blocks of poly(ethylene glycol-*stat*-propylene glycol) with about 700 g mol^{-1}), respectively. The initiators and emulsifiers under consideration are representative for systems employed typically in heterophase polymerizations as charged as well as uncharged, hydrophobic as well as hydrophilic, and monomeric as well as polymeric compounds are considered. The emulsifier concentration is in any case above the critical micelle concentration, but the number of micelles is different because the cmc for a given surfactant depends on the type of initiator as increasing ionic strength (in the case of KPS) and interactions of emulsifiers with poly(ethylene glycol) chains (such as in the case of PEGA200) influence the aggregation behavior of surfactants.[27−33] But for the present experimental study it is more important that at the beginning of the reaction micelles are present. Exclusively styrene was used in this study as it can be considered as “standard” monomer for investigations of polymerization reactions. Both restrictions regarding the kind of monomer and the emulsifier concentration will be lifted in forthcoming investigations. No redox initiator systems have been applied, and nevertheless polymerization was observed. This is to the best of the authors’ knowledge the first report on the applicability of common initiators for radical polymerizations such as AIBN and KPS in nonredox systems at temperatures as low as 25 °C. The initiator concentration was in any case higher than or close to the solubility in water or styrene; thus, the dissolved amount of initiator was constant during the duration of the polymerization.

Experimental Section

Materials. Styrene (99% purity), KPS (99+% purity), and tetrahydrofuran (99+% purity, THF), all from Sigma-Aldrich, sodium dodecyl sulfate (ultrapure for electrophoresis) from Karl Roth GmbH (Karlsruhe, Germany), and cetyltrimethylammonium bromide (without any specified purity) from Ferak (Berlin, Germany), TEGO LA-S 687 (gift from Tego Coatings and Ink Additives, Essen, Germany, LAS), and Igepal CO880 (gift from Rhodia Curbevoie, France) were all except the monomer used as received. The styrene was distilled under reduced pressure to remove inhibitors and stored in a refrigerator. Prior to use, the monomer was checked regarding oligomer formation during storage by instilling a drop into an excess of methanol. Only oligomer-free monomer was used. AIBN (pure, Fluka) and BPO (70% with remainder water, Aldrich) were both recrystallized from methanol before use.

The symmetrical poly(ethylene glycol)-azo-initiator with a molecular weight of the poly(ethylene glycol) chains of 200 g mol^{-1} (PEGA200) was prepared as described elsewhere.[34] The deionized water was taken from a Seral purification system (PURELAB Plus) with a conductivity of 0.06 μS cm^{-1} and degassed prior to use.

Polymerizations. All polymerizations were carried out at 25 °C with the following recipe, if not otherwise stated, based on mass units despite varying recipe components: 100 g of water, 6 g of styrene, 1 g of stabilizer, and 0.6 g of initiator. The batchwise emulsion polymerizations were carried out either in an all-glass reactor equipped with stirrer, reflux condenser, nitrogen inlet and outlet, and heating jacket to control the temperature or in a reaction calorimeter CPA200 (ChemiSens AB, Lund, Sweden) made of a material combination of glass (reactor walls) and stainless steel (316 SS for bottom, lid, and stirrer) according to standard procedures. Polymerizations were also conducted with a rotational thermostat VLM20 (VLM GmbH, Leopoldshöhe, Germany) in glass vials with PTFE caps for 36 h. The mixing is due to end-over-end rotation with about 15 rpm. For these polymerizations the overall reaction volume was reduced by a factor of 10. For the polymerizations with periodic sampling the initiator concentration was slightly reduced to 0.04 g per 10 mL of water.

The following prescription exemplary details the experimental procedure in the rotation thermostat. All ingredients were added in the following order: 10 g of water (0.556 mol), 100 mg of SDS (3.47×10^{-4} mol), 635 mg or 670 μL of styrene monomer (6.1×10^{-3} mol), and 60 mg of KPS (2.22×10^{-4} mol) in a glass vial (Duran glass, Schott, Germany) of about 15 mL volume (i.d. 12 mm, o.d. 16 mm, height 160 mm). Immediately before adding the ingredients, the empty vial was purged with nitrogen for approximately 5 min. Then the glass vial was screw closed with a Teflon sealing and placed in the rotation thermostat at temperature of 25 °C, and the rotation speed was set to about 15 rpm. In the rotation thermostat in use 24 vials could be placed simultaneously. After certain time intervals the rotation thermostat was stopped, and a vial was withdrawn for analytics as described below. After about 10−12 h the grayish emulsion starts to show a bluish appearance, indicating the formation of latex particles with diameters below 100 nm.

Characterizations. All latex samples taken to characterize the course of the reaction regarding, conversion, average particle size, and molecular weight had to be processed immediately. This means immediately after periodic sampling the determination of the solids content and the measurement of the average particle size were done, and getting samples for molecular weight analysis, a few drops of the dispersion were instilled into an excess of acetone to coagulate the dispersion and to precipitate the polymer. All latexes were characterized regarding the solids content (FG) with a HR 73 halogen moisture analyzer (Mettler Toledo, Giessen, Germany) and the average particle size (D_i, intensity-weighted average particle size) by dynamic light scattering (DLS) with a NICOMP particle sizer (model 370, NICOMP particle sizing systems, Santa Barbara, CA). Transmission electron microscopy (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 was employed to deposit the particles on the grid.

Molecular weight distributions (MWD) were determined by gel permeation chromatography (GPC) that was carried out by injecting 100 μL of about 0.15 wt % polymer solutions in a Thermo Separation Products setup 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-SD plus spherical polystyrene gel (average particle size 5 μm) having pore sizes of 10^3, 10^5, and 10^6 Å. This column set allows a resolution down to molecular weight less than 500 g mol^{-1}. Molecular weight distributions were determined on the basis of polystyrene standards, and the weight- and number-average molecular weight, M_w and M_n, respectively, were calculated according to standard procedures.

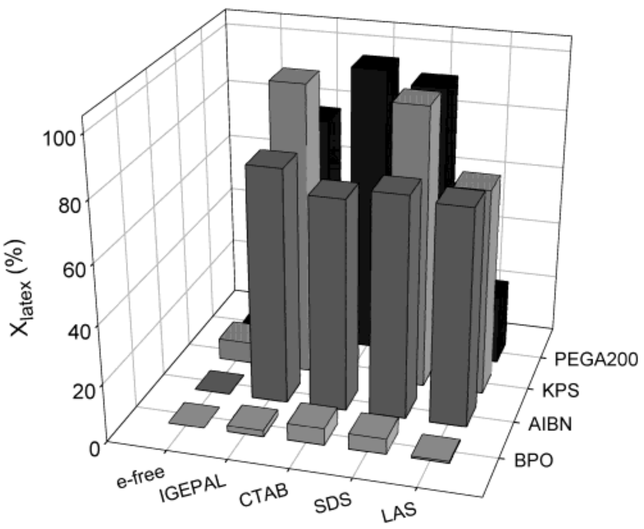

Figure 1. Final conversion for aqueous heterophase polymerizations of styrene with various initiator−emulsifier combinations; 25 °C; 36 h, rotation thermostat; recipe: 10 g of water, 100 mg of stabilizer, 635 mg or 670 μL of styrene monomer, and 60 mg of initiator; stabilizers: e-free, emulsifier-free; IGEPAL, IGEPAL CO880, and ethoxylated nonylphenol with a molecular weight of the poly(ethylene glycol) of about 880 g mol^{-1}; CTAB, cetyltrimethylammonium bromide; SDS, sodium dodecyl sulfate; LAS, TEGO LA-S 687 a symmetrical triblock copolymer with poly(dimethylsiloxane) middle block (about 20 siloxane units) with to side blocks of poly(ethylene glycol-*stat*-propylene glycol) with about 700 g mol^{-1}; initiators: BPO, dibenzoyl peroxide; AIBN, 2,2′-azoisobutyronitrile; KPS, potassium peroxodisulfate; PEGA200, poly(ethylene glycol)-azo-initiator with a molecular weight of the poly(ethylene glycol) chains of 200 g mol^{-1}.

Results and Discussion

During investigations of the influence of the emulsification step on aqueous heterophase polymerization prior to polymerization, it was accidently observed that an emulsion made of styrene and LAS was polymerized while standing at room temperature in the presence of initiator during less than 2 days. As this was repeatedly observed with either KPS or AIBN as initiator, it was the starting point for a comprehensive experimental study on aqueous heterophase polymerization at 25 °C. Polymerizations were carried out in the rotation thermostat for 36 h with 5 repeats for each initiator−stabilizer combination, showing that the standard deviation of the final conversion is about ±5%. Figure 1 demonstrates that polymerization up to high conversion takes place only if surfactant micelles are initially present and that the final conversion achieved after a certain period of time depends on the particular combination of initiator and stabilizer.

There is no value for the combination KPS/CTAB in Figure 1 as cetyltrimethlylammonium peroxodisulfate precipitates immediately; the system is unstable to coagulation (a huge amount of bulky coagulum is formed), but nevertheless polymerization takes place up to quite high conversion. The surfactant-free (e-free) runs lead only for KPS and PEGA200 to low conversion of 7.2 and 2.7%, respectively. These experimental data are indeed surprising as the amount of initiator decomposed by pure thermal decomposition should be in any case less than 1% (cf. Table 1), and one would not expect such comparably fast polymerizations as observed for all initiators except BPO. The I/I_0 data were calculated

Table 1. Characteristics of Selected Free Radical Initiators 25 °C

initiator	C_{wI} (M)[a]	k_{d} (s^{-1})[b]	I/I_0[c]
AIBN	2.44×10^{-3}	3.93×10^{-8}	0.9949
BPO	4.13×10^{-5}	5.24×10^{-9}	0.9993
KPS	1.85×10^{-2}	1.74×10^{-8}	0.9978
PEGA200	4.58×10^{-3}	1.49×10^{-8}	0.9981

[a] Solubility in water for AIBN from ref 35, for BPO from ref 11, for KPS from ref 36, and for PEGA200 from ref 34. [b] Decomposition rate constant calculated from Arrhenius relations given for AIBN and BPO for styrene as solvent in ref 21, for KPS for water as solvent in ref 2, and for PEGA200 in toluene in ref 34. [c] Calculated for a time of 36 h; I_0 and I are the initial and the final initiator concentration, respectively.

with I_0 as the overall concentration with respect to the amount of water despite the different solubilities of the various initiators.

The assumption that under the specific conditions of heterophase polymerization both an enhanced initiator decomposition takes place and a higher concentration of $\mathrm{R{-}M_1^{\bullet}}$ is formed can be checked by comparing the number of primary radicals generated due to "normal", thermal initiator decomposition ($n_{\mathrm{ini}} = I_0 - I$) with the number of polymer chains obtained experimentally (n_{pol} calculated from M_{n} and the amount of polymer formed). This comparison is however for heterophase polymerizations not as easy as in the case of homogeneous polymerizations for the following reasons. The heterogeneous nature of the reaction systems raises questions concerning the reference volume for the initiator concentration as well as the spatial distribution of the initiator molecules therein. For KPS this should not be an issue as it is only soluble in water and also not surface active. All other initiators are soluble in both the water and the organic phase, and partition coefficients should be considered instead of solubilities in pure phases. Partition coefficients have been determined for AIBN in stirred styrene−water mixtures, showing that at 50 °C the concentration per unit volume monomer is by more than a factor of 100 higher than in water.[8] However, both the type and the concentration of surfactant might influence the partition coefficient due to solubilization effects. Another issue is the spatial distribution of the initiators and of their primary decomposition products, especially inside objects of colloidal dimensions such as micelles or monomer swollen latex particles. The polarity of the water−micelle interface depends on the nature of the surfactant's headgroup. Experimental results show that the interface polarity at given alkyl chain length is highest for anionic (alkyl sulfates) followed by cationic (alkyltrimethylammonium halides) and lowest for nonionic (ethoxylated alkylphenols) surfactants.[37] For water as continuous phase there is a polarity gradient in such objects characterized by an increasing dielectric constant from the core to the interface. Consequently, polar molecules inside micelles locate toward the aqueous interface. This should be especially true for the decomposition products of BPO and AIBN but less for the undecomposed molecules. Exemplary, di-*tert*-butyl peroxide has a dipole moment of 0.92 D (25 °C, benzene solution),[38] whereas organic peroxyl radicals are more polar, having dipole moments of about 2.4 D.[39] As mentioned above, even the benzyl radical as the nonpolar initiating radical from BPO has a tendency to orientate toward the interface as it is surface active.[24] Isobutyronitrile a model for the primary radical derived from AIBN has a dipole moment of 3.61 D in benzene solution at 25 °C[40] and a solubility in water at 25 °C of about 0.52 M.[41] Furthermore, uncertainty regarding the estimation of the ratio $n_{\mathrm{pol}}/n_{\mathrm{ini}}$ comes from the use of the Arrhenius relations, which have been determined at higher temperatures and have to be used at 25 °C due to the lack of any decomposition data at such low temperatures. Additionally, there is compared with homogeneous polymerizations a further difficulty in heterogeneous polymerizations, where the width of the cumulative molecular weight distribution expressed as the ratio mass average to number-average molecular weight ($M_{\mathrm{w}}/M_{\mathrm{n}}$) is usually much broader. The different conditions regarding monomer and radical concentrations at the various reaction loci (continuous phase and monomer swollen particles) are the main reason for this fact. Moreover, $M_{\mathrm{w}}/M_{\mathrm{n}}$ depends on the initiator−stabilizer combination used. For instance, $M_{\mathrm{w}}/M_{\mathrm{n}}$ is about 3.3 for all combinations with AIBN but varies for all other systems investigated between 2.3 and 10, whereby the lowest and the highest value is obtained for BPO/LAS and BPO/IGEPAL, respectively. All polymerizations with BPO lead to the lowest molecular weights (M_{w} values between 10^4 and 10^5 g mol^{-1}) but for all other systems result M_{w} values above 10^6 g mol^{-1}.

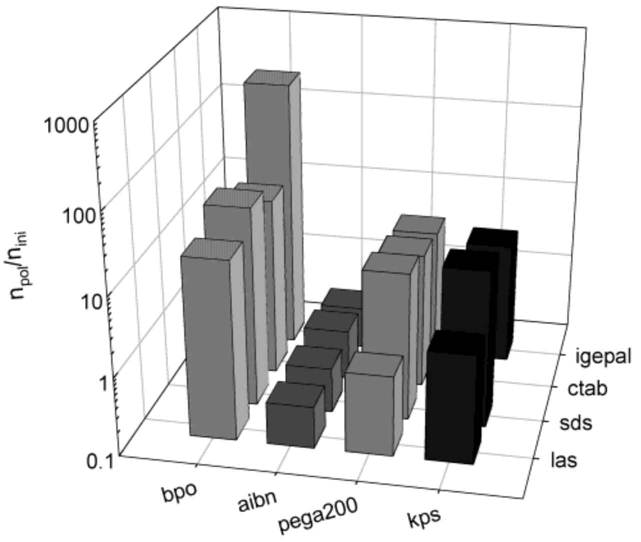

Figure 2. Ratio of the number of polymer chains formed during the polymerization and the decomposed initiator molecules for initiator−stabilizer combinations under consideration; stabilizers: IGEPAL, IGEPAL CO880, and ethoxylated nonylphenol with a molecular weight of the poly(ethylene glycol) of about 880 g mol^{-1}; CTAB, cetyltrimethylammonium bromide; SDS, sodium dodecyl sulfate; LAS, TEGO LA-S 687 a symmetrical triblock copolymer with poly(dimethylsiloxane) middle block (about 20 siloxane units) with to side blocks of poly(ethylene glycol-*stat*-propylene glycol) with about 700 g mol^{-1}; initiators: BPO, dibenzoyl peroxide; AIBN, 2,2′-azoisobutyronitrile; KPS, potassium peroxodisulfate; PEGA200, poly(ethylene glycol)-azo-initiator with a molecular weight of the poly(ethylene glycol) chains of 200 g mol^{-1}.

Despite all these difficulties and the uncertainties of the particular numerical values, the data summarized in Figure 2 for the ratio $n_{\mathrm{pol}}/n_{\mathrm{ini}}$ reveal some interesting results. Except for AIBN, the $n_{\mathrm{pol}}/n_{\mathrm{ini}}$ values are greater than 1 and indicate enhanced initiator decomposition. Clearly the largest values are determined for all polymerizations with BPO. For a given initiator the nature of the surfactant has a strong influence. This is the most distinctive for BPO, followed by KPS and PEGA200, and is the lowest for AIBN. Interestingly, the absolutely highest and lowest value is obtained for the combination BPO/IGEPAL and AIBN/IGEPAL, respectively. BPO leads not only to the highest n_{pol}/n_{ini} values but also to the largest absolute number of polymer chains generated (3.6×10^{17} per cm^3 water for the system BPO/SDS). In any case the number of polymer chains is about an order of magnitude greater than in the polymerizations with AIBN. This might be considered as another hint for the influence of interfacial forces on the initiator decomposition and/or the initiation reaction as the purely thermal initiator decomposition should result in the reverse order supposed the values of the decomposition rate constant depicted in Table 1 are applicable. For the estimation of n_{pol}/n_{ini} and in the discussion so far chain transfer reactions as possible reason for an enhanced number of polymer chains have been neglected. In aqueous heterophase polymerizations chain transfer can occur to any species present including water, stabilizer, initiator, monomer, and polymer molecules. In polymerizations with low average number of radicals per particle chain transfer to monomer is the only chain stopping event.[2] This so-called transfer limit has for styrene a value of about $5.7\ 10^6$ g mol^{-1} at 25 °C using the activation energy parameters published in ref 2. If the average molecular weight (M_n) is lower than the transfer limit, then chain stopping by termination is dominant. As the M_n values obtained are by almost a factor of 5 below this limit, chain stopping by termination should be dominant during the polymerizations considered here. In general, for radical styrene polymerization chain transfer to monomer has a higher energy of activation than propagation and becomes less important the lower the temperature[42] and even vanishes at 0 °C for bulk polymerization initiated with the redox system BPO−dimethylaniline.[43] Regarding possible chain transfer to other recipe components, the data as depicted in Figure 2 allow the conclusion that chain transfer to the stabilizers and the initiators, if it ever occurs, is very likely of only minor importance due to the large differences for the various initiators and stabilizers, respectively. Chain transfer to polymer is for styrene polymerization only appreciable at high temperatures and high conversions.[44] If chain transfer to water is important, it should take place in any experiment but especially in systems with water-soluble initiators, which, however, show no exceptional behavior (cf. Figure 2). Thus, it should be justified to neglect chain transfer events in discussing n_{pol}/n_{ini}.

The high n_{pol}/n_{ini} values for BPO allow an explanation for the low polymerization rates with this initiator as illustrated by the data depicted in Figure 1. Supposing that the decomposition of BPO is strongly enhanced at interfaces, then the high local radical concentration of either primary ($R^•$) or growing radicals ($P^•$) favors high termination rate as it scales with $[P^•]^2$.

If interfacial forces enhance the initiator decomposition, the rate of polymerization (here expressed as X_{latex} for a given time) should somehow depend on the interfacial area or the inverse average particle size. Figure 3 reveals that there are indeed specific correlations between both values for each type of initiator. It appears so as if the curves for KPS and BPO essentially describe the behavior between only two points, but in fact it is not the case as all experimental points are considered. The situation arises from the particular behavior of heterophase polymerizations where colloidal (average particle size) and kinetic effects (conversion) are overlapping, meaning that for a given initiator the average particle size does not depend much on the nature of the stabilizer but the conversion does. The values for the different stabilizers lie for each initiator on a straight line whereas the correlation regarding the kind of stabilizer is much less distinct. Interestingly, the $X_{latex}-D^{-1}$ dependence is opposing for water-soluble (KPS and PEGA200) and monomer-soluble initiators (BPO and AIBN). This is a clear hint that there are distinct differences in the mechanism of aqueous heterophase polymerizations with water- or monomer-soluble initiators although the overall polymerization kinetics between both types of initiators is not that much different as shown exemplary in Figure 4a,b. Figure 4a shows conversion−time plots for polymerizations carried out in glass vials in the rotation thermostat. The points are average values from three repeats.

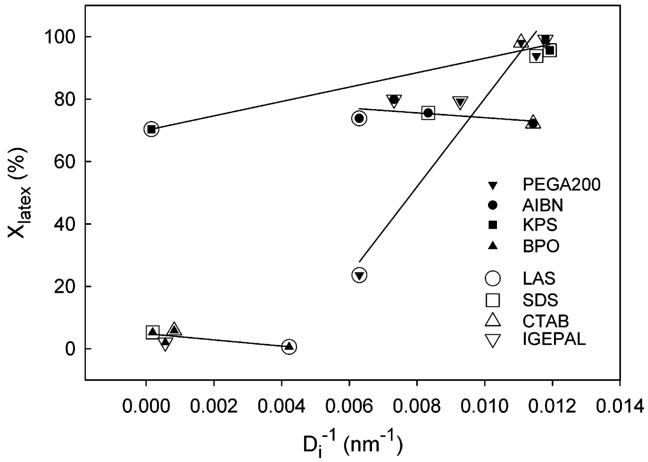

Figure 3. Final conversion (X_{latex}) in dependence on the overall final particle interface (D_i^{-1}) for different initiator−stabilizer combinations; lines are from linear regressions.

Figure 4b depicts average heat flow−time curves from three (KPS) and five (AIBN) repeats obtained in the reaction calorimeter. In both setups the general shape of the curves for AIBN- and KPS-initiated polymerizations is similar despite the faster rate for KPS. Figure 4a shows a relatively sharp increase in the conversion range between 10 and about 70%. This coincides with the polymerizations in the reaction calorimeter (Figure 4b) as the heat flow stops at conversion of 77 and 61% for KPS and AIBN, respectively. The most striking difference between both reactors is the much faster start of the polymerizations with KPS in the reaction calorimeter (1.5 ± 1.5 h) compared with glass reactors (about 8−10 h). For AIBN the polymerizations start in either reactor after more than 10 h (13 ± 4.5 h in the reaction calorimeter). Also, polymerizations in all glass reactors with mechanical stirring and reaction volumes of up to 500 mL lead to conversion time curves as depicted in Figure 4a for polymerizations in glass vials of 10 mL reaction volume in the rotation thermostat. These results prove the influence of the reactor material on aqueous heterophase polymerizations as already described in ref 45. The acceleration of the polymerization with KPS in the reactor of the reaction calorimeter containing parts made of stainless steel indicates that a redox reaction between metal atoms and peroxodisulfate dianions takes place. The enhanced initiation reaction is also reflected in the higher particle concentration or smaller particle size in the calorimeter 61.4 ± 2.8 nm vs 72.2 ± 1 nm in glass reactors. AIBN leads

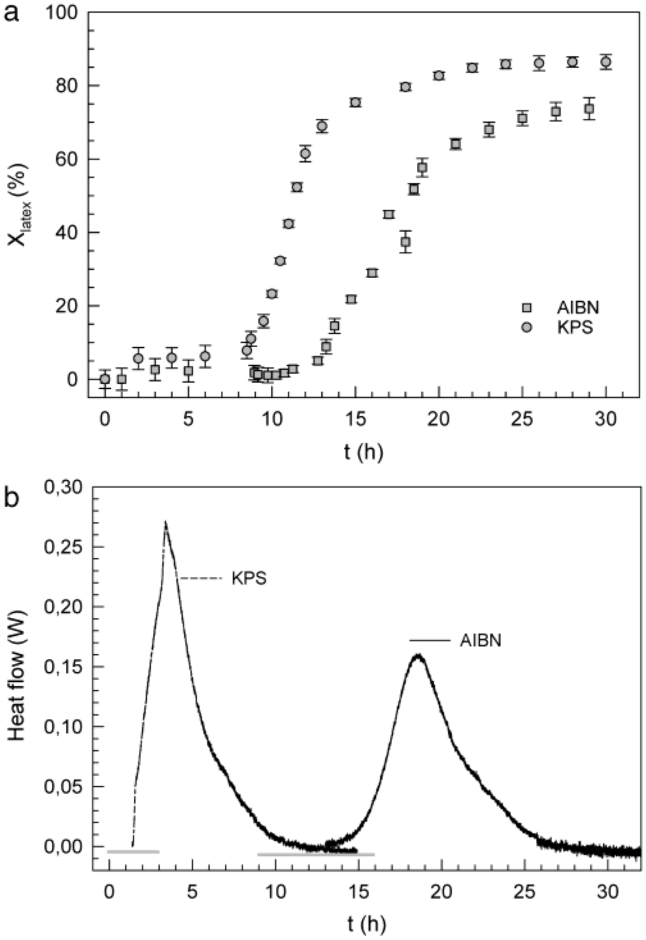

Figure 4. (a) Conversion−time curves for aqueous heterophase polymerizations at 25 °C with SDS as surfactant and AIBN or KPS as initiator in glass vials in the rotation thermostat. (b) Heat flow time curves for aqueous heterophase polymerizations at 25 °C with SDS as surfactant and AIBN or KPS as initiator in the reaction calorimeter where the reactor is made of glass and stainless steel; the gray bars indicate the scatter of the onset of the detection of heat flow.

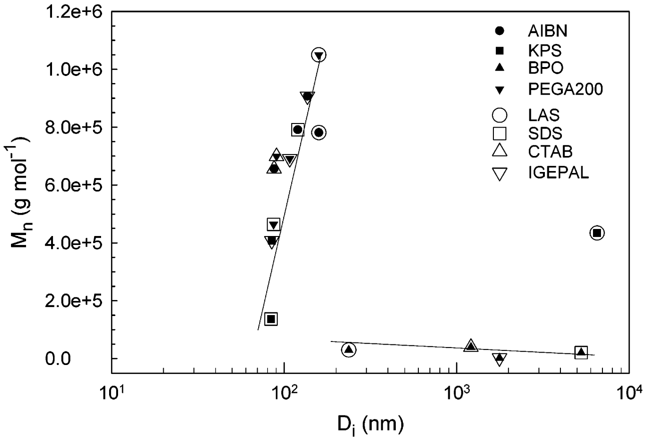

Figure 5. Change of the cumulative number-average molecular weight (M_n) with the logarithm of the final average particle size (D_i) for the initiator−stabilizer combinations under consideration.

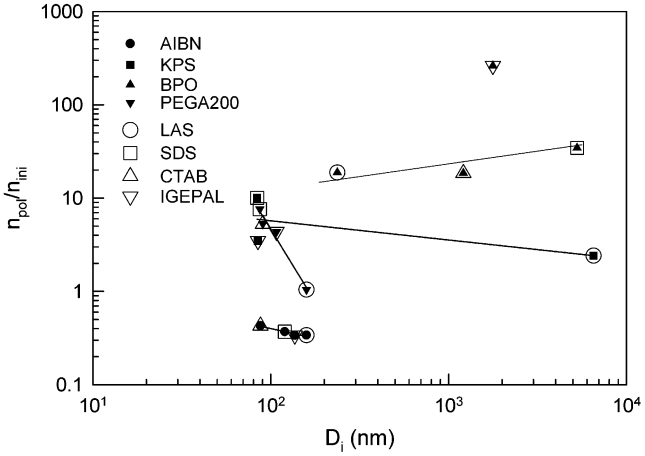

Figure 6. Ratio of the number of polymer chains formed during the polymerization and the decomposed initiator molecules (n_{pol}/n_{ini}) in dependence on the average particle size (D_i) of the final latexes for the different initiator−stabilizer combinations; the lines are from linear regressions.

in both reactor types to larger particles; however, the difference between the calorimeter and the glass reactors is smaller, 104.1 ± 1.3 nm and 109.8 ± 9 nm, respectively.

The difference between monomer- and water-soluble initiators as expressed in Figure 3 might lead to expectations that also other latex properties behave differently and thus help elucidate the peculiarities of heterophase polymerization with either lyophobic or lyophilic initiators. The importance of the dispersity (average particle size or curvature) of the main reaction loci of monomer consumption, the monomer swollen latex particles, is again expressed by the data plotted in Figures 5 and 6.

Figure 5 shows that the number-average molecular weight changes linearly with the logarithm of the average final particle size. The data points for all initiators except BPO follow within the experimental error one line, indicating that the average molecular weight increases with increasing average particle size. These experimental results for all initiators except BPO show that the cumulative number-average molecular weight is obviously determined by the monomer concentration inside the particles, which in the given particle size range increases the larger the particles.[46] Contrary, for BPO as initiator the molecular weight is determined by the average radical concentration per particle, which also increases with increasing average particle size. The outlier of the combination KPS/LAS is due to colloidal instability of this particular initiator−stabilizer combination where the hydrophobic poly(dimethylsiloxane) is of special importance. However, the specific role of LAS as stabilizer is beyond the scope of this paper and will be treated in a separate communication.

Considering the ratio n_{pol}/n_{ini}, which combines experimental results (X_{latex} and M_n) with the assumptions regarding the decomposition of the initiators, the graph vs the average particle size also reflects the unique role of BPO among all initiators under investigation (Figure 6). The position of the data point especially for KPS and PEGA200 in the graph is again influenced by overlapping kinetic and colloidal effects as discussed in context with Figure 3.

The ratio n_{pol}/n_{ini} increases for BPO whereas it decreases for all other initiators with increasing particle size. These different dependencies prove the above conclusion that the huge number of radicals generated by interface stimulated initiator decomposition (n_{ini} increases strongly with D_i^{-1}), and the high termination rate caused by it controls the behavior of the polymer-

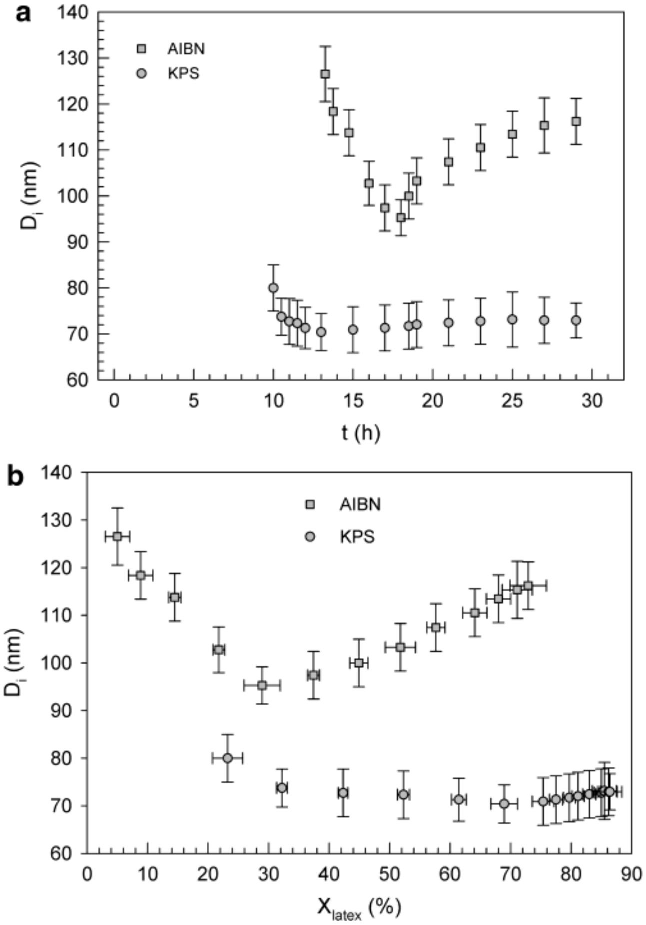

Figure 7. (a) Time development of the average particle size (D_i) during aqueous heterophase polymerizations in the rotation thermostat at 25 °C with SDS as surfactant (averaged and smoothed data from three runs). (b) Development of the average particle size (D_i) with conversion (X_{latex}) during aqueous heterophase polymerizations in the rotation thermostat at 25 °C with SDS as surfactant (averaged and smoothed data from three runs).

izations with BPO. On the contrary, n_{pol}/n_{ini} for the other systems is controlled by the propagation reaction and monomer conversion inside the latex particles.

Beside the advantage of addressing clearly the influence of interfacial forces on the decomposition of initiators in heterophase polymerizations, the low polymerization temperature offers the additional advantage of a general slow kinetics allowing comparably easy time- or conversion-dependent analysis of reaction periods where usually very fast changes take place such as at low conversions during the period of the nucleation of the first latex particles. Examples regarding the development of the average particle size (monomer swollen particles) during the polymerizations as described by the conversion−time curves in Figure 4a,b are given in Figure 7a,b.

Comparison of the same data once plotted vs time (Figure 7a) and once vs conversion (Figure 7b) allows the detection of both another difference and another common feature between water- and oil-soluble initiators. The detection of the first latex particles with the particular equipment used for DLS occurs for the hydrophobic AIBN at much lower conversion than for the hydrophilic KPS. However, the more astonishing result is the conversion at which this is possible as it is above 5% for AIBN and already about 20% for KPS. This time or this conversion means that the average particle size determined by DLS is for the first time during the course of the reaction below the micrometer range, and the dispersion changed its appearance from gray to white and bluish which is typical for polymer latexes at the given surfactant concentration. Because of the immediate measurement after periodic sampling monomer droplets, which are stabilized by the high surfactant concentration, contribute to scattering at any time before particles have been formed. After particle nucleation the surfactant is mainly adsorbed at the much larger particle interface, and the monomer drops are less stabilized and will faster cream upon the necessary dilution for the DLS measurements. The exact time when the first latex particles appear cannot be determined by this way, but it allows an estimate with an error in the order of the periodic sampling time, which is 0.5 h or 2−3% and 5−10% conversion for AIBN and KPS, respectively. Even if no particles are detectable, polymerization starts from the very beginning as the GPC data prove the presence of polymers already after 1 h of polymerization time. Parallel to the occurrence of latex particles, the molecular weight jumps from $M_n \sim 5 \times 10^3$ g mol^{-1} and $M_n \sim 1 \times 10^3$ g mol^{-1} during the prenucleation period to $M_n \sim 2 \times 10^5$ g mol^{-1} and $M_n \sim 5 \times 10^5$ g mol^{-1} after latex particles have been nucleated for KPS and AIBN, respectively. Another extremely interesting result is the difference in the MWD between both initiators during the prenucleation period as initiation with KPS leads to monomodal MWD whereas with AIBN bimodal MWD are obtained. The bimodal MWD for AIBN obviously reflects the two polymerization loci water phase (low molecular weight, $M_n \sim 1 \times 10^3$ g mol^{-1}) and monomer droplets (high molecular weight, $M_n \sim 1 \times 10^5$ g mol^{-1}). The low molecular weight portion of the cumulative MWD increases from 28 wt % after 1 h to 48 wt % after 3 h of polymerization time, indicating increasing importance of the aqueous phase as reaction locus during the prenucleation period. In contrast to these results, the MWD for the polymerizations with KPS does not change during the prenucleation period.

These results obviously contradict the micellar nucleation theory, which is frequently used to explain results for styrene emulsion polymerization[2,3] but can nicely be explained within the frame of moderner theories based on general nucleation theories such as the aggregative nucleation theory for heterophase polymerization based on the classical nucleation theory.[47−49] In brief, according to these considerations, particle nucleation requires also in emulsion polymerization the buildup of a supersaturation of the nucleating species, and hence, it is governed by the molecular weight and concentration of these species, which are oligomers. The supersaturation is influenced by the nature of the end group, which explains that the hydrophobic oligomers with the isobutyronitrile end group nucleate at lower conversion than the more hydrophilic oligomers with sulfate end groups. However, a detailed discussion of the particle nucleation in this particular case of heterophase polymerizations is beyond the aim of this contribution and needs further experimental investigations. Because of the lower temperature and the lower rate of initiation, the particles prenucleation period is extended and thus enables more favorable investigation conditions. Furthermore, the particle size distribution is quite broad as the TEM pictures in Figure 8 show, indicating also an extended nucleation period or multiple nucleation events.

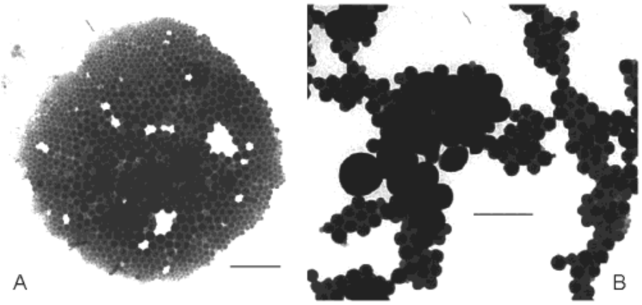

Figure 8. TEM photographs of final latex samples prepared at 25 °C in all-glass reactors with the initiator–stabilizer combinations AIBN/SDS (A) and AIBN/LAS (B). The bars indicate 500 nm.

Conclusions

The experimental results presented clearly show that radical heterophase polymerization of styrene are promoted in micellar aqueous media at room temperature in the presence of nonredox initiators. This allows performing radical heterophase polymerizations at much lower temperatures than usually expected, considering only the pure thermal decomposition of common initiators such as KPS or AIBN. The supposition is fair that the polymerization is promoted by interfacial energy as the presence of surfactant micelles is needed. Assuming an interfacial tension γ_{mic} of 10 mN m^{-1} and a diameter (D_{mic}) of 5 nm, which are values applicable for styrene swollen micelles, the interfacial energy of a micelle ($e_{\mathrm{IF,mic}} = \gamma_{\mathrm{mic}}\pi D_{\mathrm{mic}}^2$) is about a factor of 200 greater than the thermal energy ($E_{\mathrm{therm}} = k_{\mathrm{B}}T$) at 25 °C. It is not the surface energy of a single micelle but its product with the number of micelles per unit volume (N_{mic}), $E_{\mathrm{IF,mic}} = e_{\mathrm{IF,mic}}N_{\mathrm{mic}}$, corresponding to the curvature times interfacial tension or the Laplace pressure of the particular colloidal system,[50] that has to be considered. The experimentally observed dependence of the conversion rate on the total surface area (Figure 3) supports this assumption. However, the crucial issue is the availability of this energy to influence partial reactions such as primary radical formation or initiation. At the moment detailed conclusions regarding the particular mechanism are not possible, but the experimental data show that the reaction is strongly influenced by the nature of the initiator–stabilizer combination. Further investigations are concentrated on investigation to follow the initiator decomposition, to determine the nature of end groups, to vary the concentration of the reactants, and to include other monomers than styrene. The detailed analytics regarding the rate of initiator decomposition and the nature of the end groups is complicated due to the high amount of surfactant in the system as any method to remove the surfactants is prone to remove also oligomers.

The investigation of radical heterophase polymerizations at temperatures where the rate of initiation is low allows not only the recognition of differences in the polymerization behavior between monomer- and water-soluble initiators, which are not observable under conventional conditions at higher temperatures. Moreover, it allows a more detailed insight into the mechanism of particle nucleation also for polymerizations with surfactant concentrations above the critical micelle concentration where at elevated temperatures the particle nucleation is extremely fast.

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