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RAFT Agent Concentration in Polymer Particles during Emulsion Polymerization

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ABSTRACT: A novel experimental setup to measure the diffusion and the concentration of light-absorbing molecules in particles of polymer dispersions is described. This method allows for instance quantification of the diffusion of hydrophobic reversible addition-fragmentation chain transfer (RAFT) agents from the monomer phase into the polymer particles during ab initio emulsion polymerization. The results clearly show that the diffusion of the RAFT agents strongly depends on their water solubility. This explains their influence on the kinetics of RAFT aqueous heterophase polymerization. Moreover, the retaining or the loss of the color of the RAFT agents after addition of different initiators recorded by this method gives direct experimental evidence that primary initiator radicals enter polymer particles.

Introduction

Reversible addition-fragmentation chain transfer polymerization is one of the most versatile methods of controlled radical polymerization (CRP).[1] The mild conditions required for the RAFT process and more pronounced consequences of the compartmentalization, i.e., higher polymerization rate and molecular weight, in RAFT heterophase polymerization makes this method a suitable candidate for CRP in aqueous heterophase systems. However, there are serious issues of stability and efficiency accompanying the RAFT process in such systems. Several groups have pointed at the influence of the hydrophobicity of the RAFT agent on the kinetics of the heterophase polymerization and the complications in control and stability of the system due to inefficient transportation of the RAFT agent to the loci of polymerization.[2−6] An instructive review regarding the difficulties one faces during the implementation of RAFT in aqueous emulsion polymerization has recently been published.[7] The authors discuss the role of the solubility of the RAFT agent (hydrophilic or hydrophobic or surface active) and state also that the transport of the RAFT agent to the polymer particles is of paramount importance. If the RAFT agent is too hydrophilic, the chain transfer reaction is restricted for a longer period of time in the aqueous phase with the consequence of long retardation periods.[5] Contrary, aqueous heterophase polymerizations with highly water-insoluble RAFT agents face the problem of the transport of the RAFT agents through the water phase, and hence, a considerable portion of the reaction takes place inside the monomer phase.[5−8] Even if the RAFT agent is surface-active, the control can be poor as it is distributed among water, monomer, and interfaces.[9] In this discussion the authors in ref 7 conclude that facilitating the transport of hydrophobic RAFT agents by water-soluble organic cosolvents into the particles should, although not industrially viable, be the method of choice to create an ideal system for aqueous RAFT heterophase polymerization.

The level of control and the rate of polymerization are determined by the concentration of the controlling agent and its ratio to the primary radicals at the loci of polymerization. In heterophase systems and especially in ab initio emulsion polymerization the concentration of the reactants in the various phases mainly depends on their solubility and partitioning in each of these phases. Because of the multiphase nature of ab initio heterophase polymerizations, it is very difficult to experimentally determine the concentration of the reactants at the main loci of polymerization, i.e., inside the polymer particles.

In a preceding systematic investigation of ab initio emulsion polymerization of styrene mediated by the RAFT agents listed in Table 1, a strong influence of the hydrophobicity of both the RAFT agents and the initiators was observed.[8] These results showed that a higher control was obtained for the less hydrophobic RAFT agents. This can be explained by the assumption that the less hydrophobic RAFT agent can be transported to the polymer particles with higher rate; hence, it provides a higher ratio of RAFT agent/radical concentration and a higher level of control at the main reaction locus. For the RAFT agents listed in Table 1 it is reasonable to assume the following order of hydrophobicity: CDB > PhEDB > BDB > BDA.

However, there are no data available confirming this assumption. Therefore, the water solubility of these RAFT agents was roughly estimated using a relation between the water solubility (S_W) and octanol−water partition coefficients (K_{OW}) as described by Yalkowsky and Banerjee.[10] This procedure requires, first, the estimation of the K_{OW} by fragment constants for each structural component and, second, a proper relation between S_W and K_{OW}. With the data for calculating K_{OW} and a S_W−K_{OW} relation for esters,[10] approximate water solubility values that are obtained for BDA, BDB, PhEDB, and CDB are 14, 1.2, 0.3, and 0.05 mM, respectively. Again, it must be emphasized that this is a very rough estimation which only confirms the trend of water solubility of these compounds.

The introductory discussion has shown that experimental data regarding the transport of hydrophobic RAFT agents from the monomer phase to the latex particles would be helpful in order to gain more insight

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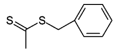
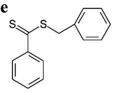
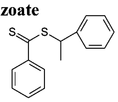
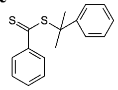
Table 1. Structures of Various Thiocarbonylthio Compounds as RAFT Agents

(a) Benzyl dithioacetate **(BDA)**		**(b) Benzyl dithiobenzoate** **(BDB)**	
(c) Phenyl ethyl dithiobenzoate **(PhEDB)**		**(d) Cumyl dithiobenzoate** **(CDB)**	

into the mechanism of RAFT aqueous heterophase polymerization. The aim of this contribution is to describe a method that allows the experimental determination of the diffusion of the RAFT agents from the monomer phase through the aqueous phase into the latex particles. The availability of such an experimental procedure is of importance for further investigations of the kinetics of both ab initio and seeded RAFT emulsion polymerization.

Experimental Section

Materials. Water 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′-Azobis(2-methyl-*N*-(2-hydroxyethyl)propionamide) (VA-086 from Wako), potassium peroxodisulfate (KPS from Fluka), and sodium dodecyl sulfate (SDS from Roth) were both used as received. Poly(ethylene glycol)-azo-initiator (PEGA200) with an average molecular weight of 569 g/mol was synthesized as described elsewhere.[11] Styrene, methyl methacrylate, and ethylbenzene (all from Aldrich) were distilled under reduced pressure. Polystyrene nanoparticles (~34 nm diameter) were synthesized through emulsion polymerization of styrene as described elsewhere[12] and were dialyzed extensively to remove all water-soluble components including surfactants. All the RAFT agents—benzyl dithioacetate (BDA), benzyl dithiobenzoate (BDB), phenyl ethyl dithiobenzoate (PhEDB), and cumyl dithiobenzoate (CDB)—were synthesized and purified as described in ref 1.

Instruments. *UV–vis Spectroscopy Investigations*. A special port for a UV–vis immersion probe from Hellma (Müllheim/Baden, Germany) with an optical path length of 10 mm connected with a glass fiber optics to a UV–vis spectrometer Specord 30 (Analytik Jena GmbH, Germany) was used for all the measurements regarding the phase transfer. The investigations were carried out in a special homemade double-jacketed all-glass reactor equipped with condenser, mechanical stirrer, heating and cooling jacket, and thermostat. An extra neck on the side of the reactor allowed placing the special port for the UV–vis immersion probe (Figure 1).

Ab Initio Emulsion Polymerizations. The polymerizations were carried out in double-jacketed four-necked all-glass reactors equipped with heating and cooling thermostats, nitrogen inlet, condenser, and mechanical stirrer. The latexes were characterized regarding solids content with a HR73 halogen moisture analyzer (Mettler Toledo). Number-average molecular weights 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 setup being equipped with ultraviolet (UV) (TSP UV1000) and refractive index (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. This column set allows a resolution down to molecular weights less than 500 g mol^{-1}. Molecular weights and molecular weight distributions were calculated on the basis of polystyrene standards (between 500 and 2×10^6 g mol^{-1} from PSS, Mainz, Germany).

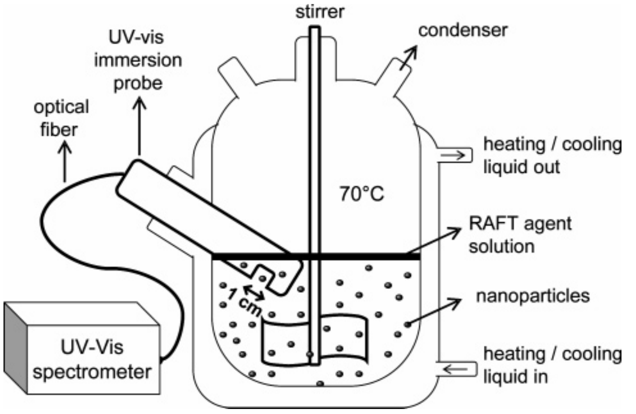


Figure 1. Schematic drawing of the experimental setup used for the quantification of the uptake of RAFT agents by latex particles; the reactor is filled with a dispersion of polystyrene nanoparticles (the size of the particles should be small enough to allow the application of a high enough particle concentration to clearly see the absorption increase caused by the RAFT agent inside the particles despite all the scattering caused by the latex). Stirring is adjusted so slow that no emulsification of the RAFT agent solution, which is placed on top of dispersion, takes place. The absorption is measured by a UV–vis immersion probe relative to the turbidity caused by the neat dispersion at given temperature. For details see experimental part.

Procedure. *UV–vis Spectroscopy Investigations*. The reactor was filled with 200 g of polystyrene dispersion containing polystyrene nanoparticles with solids content of 0.425 wt % (or 0.85 g of PS seed in total), corresponding to a total seed particle number of 3.6×10^{16} or 1.8×10^{14} per cm^3 of water. This combination of size and concentration of the seed particles causes a level of turbidity in the reactor, which is optimum for absorption measurements. This means the concentration of particles is on the one hand high enough to take up detectable amounts of organic compounds and is on the other hand low enough not to cause a too high turbidity. Such a condition is only achievable with very small particles. The dispersion was heated to 70 °C, and the absorption baseline was measured after thermal equilibration. This procedure ensures that almost all changes measured are due to the sorption process. The stirrer speed was adjusted to about 50 rpm, which is just enough to sufficiently mix the seed particles but not to disperse the organic phase that is slowly placed on top of the dispersion inside the reactor after the thermal equilibration is achieved. The organic phase is a solution of 2×10^{-4} mol RAFT agent in 0.74 g of styrene (or 0.71 g of ethylbenzene or 0.77 g methyl methacrylate). The applied amount of RAFT agent solution is lower than the necessary amount for equilibrium swelling of the latex particles in order to achieve the complete uptake of the organic phase during the sorption experiments. The absorption was measured every 5 or 10 min in the wavelength range between 300 and 800 nm. After the RAFT agent solution was completely absorbed into the polymer particles and no solution was left on top, and after a period of equilibration, 2 g of an aqueous solution of initiator (79.6 mM) was added to the dispersion in order to start the polymerization.

Ab Initio Emulsion Polymerizations. 70 g of water and 4 g of aqueous solution of SDS (5 wt %) were charged into the reaction vessel. This solution was stirred and heated to 80 °C for 30 min while purging nitrogen, and then the solution of RAFT agent in styrene was added. After 5 min of thermal equilibration, the solution of PEGA200 initiator in 10 g of water was added and the reaction started. The nitrogen flow, the 80 °C temperature, and the 300 rpm stirring speed were maintained for the whole course of polymerization reaction until the gravimetric measurements indicated the full conversion. Samples were taken at specific intervals. A portion of the sample was analyzed for the solids content by the moisture analyzer, and another portion of each sample was dropped into excess amount of petroleum ether to precipitate. After separa-

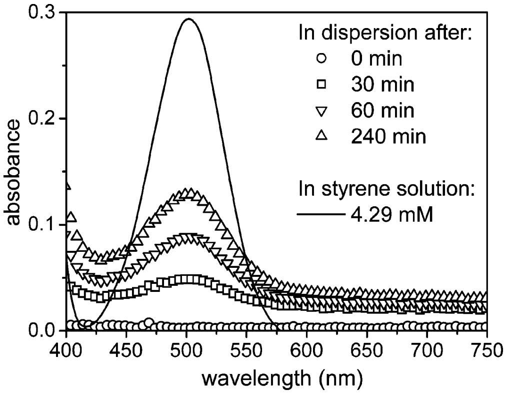


Figure 2. Absorbance of light by RAFT agent BDB in styrene solution (solid line) and in aqueous polystyrene dispersion at different times (symbols).

tion of polymer and drying it in the oven, it was prepared for GPC analysis.

Results and Discussion

Since the RAFT agents are colored because of the n → π* forbidden transition of their C=S group, UV−vis spectroscopy was presumed to be a proper technique for measuring the concentration of the RAFT agent in the aqueous phase. But all attempts were unsuccessful to get quantitative data as they only showed that the RAFT agents under consideration have no or negligible solubility in water. These experiments were carried out in a UV cuvette by placing solutions with a known concentration of RAFT agent in styrene on top of pure water and measuring the absorbance over a large visible range (300−800 nm) every 10 min. Even though the optical path through the water phase was as long as 50 mm, no absorbance could be detected. Replacing the pure water with a surfactant solution did not enhance the absorbance. However, while following the absorbance through the monomer phase an increase in the RAFT agent concentration was measured in that phase with time. This means that at least styrene diffuses into the water phase, but no trace of RAFT agent could be detected.

These results were puzzling since the polymerization data clearly show that all these RAFT agents are able to enter the particles and lead to some level of control. During a batch ab initio RAFT polymerization with very low monomer content and slow stirrer speed, an observation was made that after nucleation the dispersion became colorful. The idea was born to use a diluted dispersion of small-sized particles instead of pure water or surfactant solution and simulate the typical conditions of heterophase polymerization as similar and as simple as possible. A novel experimental setup was designed with an in-line UV−vis probe allowing time-dependent measurement directly inside the dispersion as sketched in Figure 1 and described in detail in the Experimental Section.

The method as described above proved to be effective because the diffusion of RAFT agents into the dispersion could be easily followed. As an example, Figure 2 shows the increase in the absorbance of the RAFT agent in the dispersion with increasing time. The coincidence with the absorption spectrum of the particular RAFT agent (BDB) in a styrene solution shows that the RAFT agent is located inside the dispersion also in a styrene-like environment, which is the swollen particle phase. That the particles are swelling during the sorption process is shown by the increasing baseline in the absorption spectra. The presence of polystyrene nanoparticles proved to be crucial because in a control experiment under the same conditions but without latex particles, no absorbance corresponding to the RAFT agent was measured. Therefore, we can conclude that the RAFT agent diffuses along with the monomer into the polymer particles and that at any time the BDB concentration in the continuous aqueous phase is extremely low.

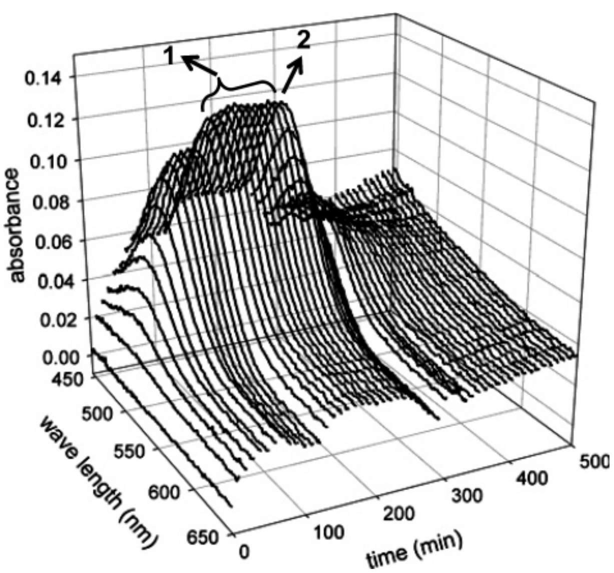


Figure 3. Absorbance of RAFT agent BDB in aqueous polystyrene dispersion during all the stages of sorption, equilibrium, and polymerization: (1) equilibrium period; (2) addition of KPS initiator.

The experimental setup is not restricted to follow only the sorption but allows also in-line monitoring of further reactions. Figure 3 shows an example where after the sorption process the polymerization was started by initiator additions. All the different stages of the whole process, which are sorption and swelling of the particles with a BDB in styrene solution, equilibration of the swollen particles, and polymerization after KPS addition, are clearly detectable.

After addition of KPS, the absorbance decreases with time and eventually the dispersion becomes colorless. The color loss indicates that the chromophore, that is the RAFT agent, undergoes degradation. This is not expected to be caused by polymerization or exchange of the benzyl leaving group. The hydrolysis of these RAFT agents is also not probable since it is inside the hydrophobic particles and moreover, the dithiobenzoates are proven to be stable under acidic conditions.[13] Therefore, the decoloration effect is believed to be the result of a side oxidation reaction by sulfate ion radicals. These radical ions possess a high redox potential of 2.6 eV,[14] and several examples are known for oxidation reaction of organic sulfur compounds by persulfate.[15]

For the purpose of comparison further experiments were carried out to verify this hypothesis as summarized in Figure 4 and Figure 5. In the first one, where styrene was replaced by ethylbenzene polymerization could not take place anymore, but the rate of decoloration was practically unchanged. However, in the second comparison experiment where additionally KPS was substituted with VA-086, which is a water-soluble azo-initiator the decoloration rate is drastically reduced. It is to mention here that also for other initiators leading to carbon-

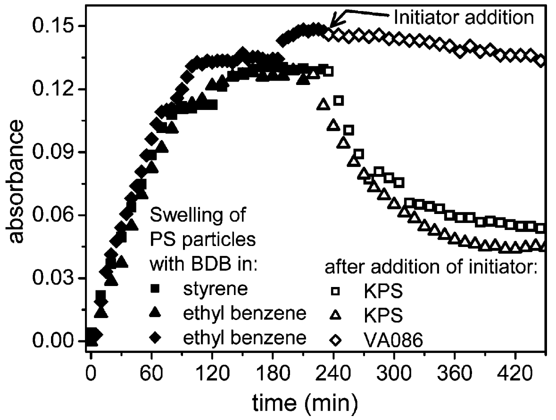


Figure 4. Development of the light absorbance by RAFT agent BDB in polystyrene dispersion with time before and after the addition of initiators KPS and VA-086. Organic solvents were styrene and ethylbenzene.

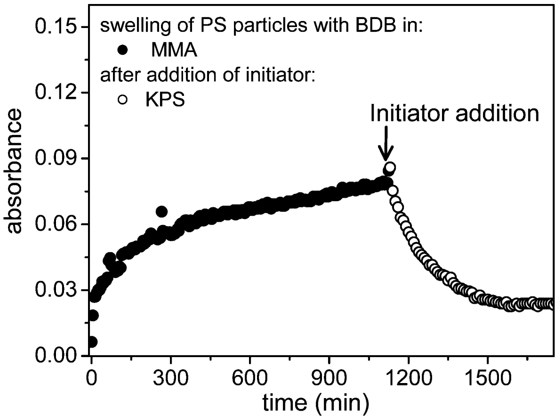


Figure 5. Development of the light absorbance by RAFT agent BDB in polystyrene dispersion with time before and after the addition of initiator KPS. Organic solvent was MMA.

centered radicals such as 2,2′-azobis(isobutyronitrile) or poly(ethylene glycol)-azo-initiators no decoloration of the RAFT agent containing particles was observed during polymerization.

Even if styrene is replaced by MMA, which has much higher water solubility, the decoloration takes place with peroxodisulfate initiator. This indicates that the water solubility of the monomer does not influence the occurrence of the decoloration but influences the decoloration rate (cf. Figure 5).

An evaluation of the absorbance data after initiator addition as pseudo-first-order reaction as described in ref 16 yields for the combination KPS/ethylbenzene a reaction rate constant of 2.80×10^{-5} s^{-1}, which is quite close to the decomposition rate constant for KPS at 70 °C (2.2×10^{-5} s^{-1}).[17] In contrast, for the combination VA-086/ethylbenzene the pseudo-first-order reaction rate constant is almost 2 orders of magnitude lower (5.54×10^{-7} s^{-1}) and also is much less than the decomposition rate constant of VA-086 (4×10^{-6} s^{-1}, at 70 °C). These results are of special meaning for controlled radical emulsion polymerizations via RAFT as it proves the possibility of the degradation of RAFT agents by peroxyl radicals not only in the water phase but also inside the hydrophobic environment of the latex particles. Contrarily, azo-initiators obviously contribute mainly to the initialization of the RAFT process,[18] and side oxidation reactions, which can occur if oxygen is not completely excluded, are only of minor importance.[19]

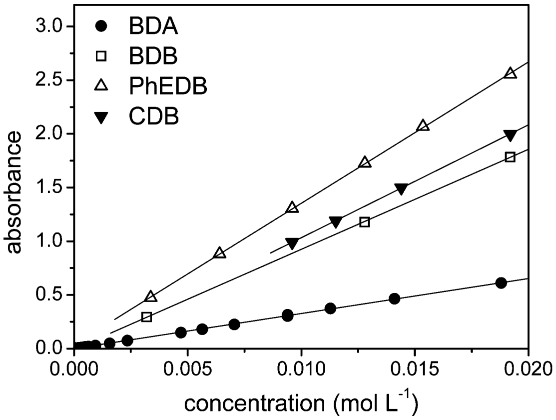


Figure 6. Maximum absorbance vs concentration for various RAFT agents in styrene solution (the slope determines the extinction coefficient).

Already, a qualitative evaluation of the experimental data depicted in Figure 4 leads on one hand to the unambiguous conclusion that the decoloration is not caused by carbon-centered radicals but only by peroxo radicals. On the other hand, these data prove that peroxo and hence primary initiator radicals enter the latex particles where BDB is located, and decoloration takes place. Obviously, surface activity as postulated in ref 20 is no prerequisite to enter latex particles. Another example confirming this conclusion comes from polymerization experiments with microcapsules as described in ref 21. The authors loaded hollow polyelectrolyte capsules of a few micrometers diameter with styrene sulfonate monomer and carried out KPS-initiated polymerizations. The monomer inside the capsules was polymerized as well as the monomer in the continuous phase. Neither the primary initiator nor the oligomeric radicals of styrene sulfonate are surface active, but they succeeded to pass a thick layer of polymer wall with a few nanometers thickness in order to start the polymerization inside the capsules; therefore, these results confirm the above conclusion drawn from our experiments with latex particles.

A comparison of the data sets presented in Figures 4 and 5 reveals that the rate of sorption of the RAFT agent BDB into the polystyrene particles is significantly slower when it is dissolved in MMA instead of styrene. Although MMA is a good solvent for BDB and has higher water solubility than styrene, the rate of its transportation into the particles is significantly slower. An explanation might be that MMA is too hydrophilic to transport the RAFT agents as effective as the other solvents. This suggests that a complex relation between all of the participating components—the polymer, the solvent, and the hydrophobic organic compound such as the RAFT agent—influences the rate of sorption.[22] This is of particular importance in kinetics of heterophase polymerization where the reaction components must be absorbed into the polymer particles as the main loci of polymerization.

To evaluate the influence of the hydrophobicity of the RAFT agents, the sorption experiments were carried out with all of the RAFT agents given in Table 1. The absorbance values were converted to concentrations assuming the validity of Lambert−Beer's law with extinction coefficients determined in styrene as solvent. The linear absorbance−concentration plots depicted in Figure 6 prove the applicability of Lambert−Beer's law at least for the RAFT agent solutions. As it is not

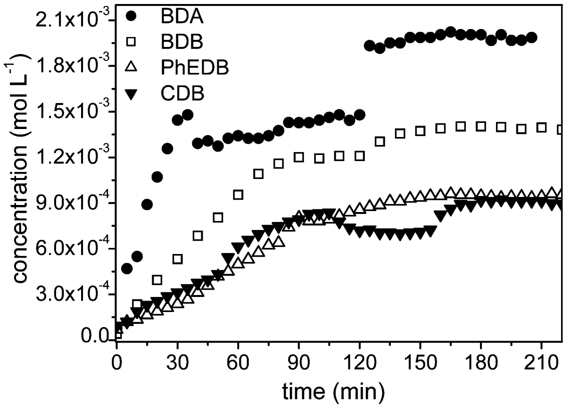


Figure 7. Concentration of various RAFT agents absorbed in the dispersion of polystyrene nanoparticles in water at different times.

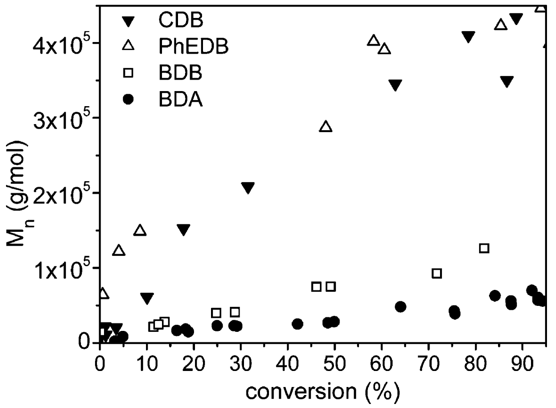


Figure 8. Number-average molecular weight vs conversion during ab initio emulsion polymerization of styrene with various RAFT agents initiated with PEGA200. Final average PDI values for BDA, BDB, PhEDB, and CDB are respectively 1.35, 1.7, 2.2, and 3.0.

possible to measure exactly the extinction coefficient of the RAFT agents in the polystyrene dispersions, the extinction coefficients measured in pure styrene solutions have been employed for calculation. This is considered to be a good approximation because the RAFT agents are believed to be only present inside the particles. These values regardless of containing errors such as scattering effects can be very well used to characterize the uptake of different RAFT agents in the polymer particles. The data in Figure 7 despite all the jumps, which are caused by the electronics of the spectrometer, show that the nature of the RAFT agent has a strong influence on both the sorption rate and the equilibrium concentration in the particles. As expected the sorption rate is higher in the order of BDA > BDB > PhEDB ≈ CDB. In Figure 7, it can be seen that 30 min after adding the RAFT agent solutions the concentration for BDA in the polymer particles is at least twice as high as that for BDB and 4 times higher than that for both PhEDB and CDB.

The sorption order of the RAFT agents and also the small difference for CDB and PhEDB matches very well with the experimental results obtained in ab initio emulsion polymerizations as elaborated in ref 23 and illustrated by the data put together in Figure 8. As smaller number-average molecular weight of polymer latex indicates higher concentration of RAFT agent inside polymer particles, the order of number-average molecular weights in Figure 8 for different RAFT agents (CDB ≈ PhEDB > BDB > BDA) corresponds to their concentration in the polymer particles (BDA > BDB > PhEDB ≈ CDB).

Table 2. Wavelengths of Maximum Absorbance (λ_{max}) and the Extinction Coefficients Obtained for Different RAFT Agents

RAFT agent	λ_{max} (nm)	extinction coeff (L/(mol cm))
BDA	456	32.635
BDB	502	93.084
PhEDB	503	131.632
CDB	528	105.088

Conclusion

The experimental results obtained prove the usefulness of the developed experimental setup and procedure based on in-line UV−vis spectroscopy measurements for the quantitative investigation of the sorption of RAFT agents in polymer particles under typical conditions of aqueous heterophase polymerization. To do so, the size and concentration of polymer particles must be optimized. The optimum conditions for polystyrene latexes in our particular setup have been found to be ~34 nm particle diameter with the concentration of 1.8×10^{14} particles cm^{-3}. However, for particles and continuous phases with different refractive indices the optimum conditions have to be determined anew.

The experimental results prove the dependence of the diffusion rate of hydrophobic RAFT agents from the monomer phase to the particles on the hydrophobicity of the particular RAFT agent as well as on the water solubility of the monomer. For a given monomer the RAFT agents diffuse through the aqueous phase into the polymer particles in the order BDA > BDB > PhEDB > CDB. This order corresponds also to the molecular weight control observed in ab initio batch styrene emulsion polymerizations.

The degradation of the RAFT agent by addition of KPS initiator provides unambiguous evidence that even extremely hydrophilic primary radicals, such as sulfate ion radical stemming from the KPS initiator, can enter the polymer particles without necessarily having propagated and reached a certain chain length.

In contrast to azo-initiators, peroxodisulfate leads via side oxidation reactions to a degradation of the RAFT agents inside polymer particles. However, this does not mean that polymerizations initiated with peroxodisulfate are uncontrolled. Contrarily, ab initio RAFT emulsion polymerization of styrene initiated with KPS appeared to be quite controlled.[8] Most likely, there is a competition between the controlled chain growth via the RAFT equilibrium and the destruction of the RAFT agent by side oxidation reactions. As the average radical concentration per latex particle is low, also a low concentration of the RAFT agent is sufficient for an effective control (compartmentalization effect).

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