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Experimental Reconsideration of Radical Entry into Latex Particles

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Emulsion polymerization can be generally characterized as a heterophase reaction system consisting of an aqueous phase, containing the initiator and monomer swollen colloidal polymer particles. It is commonly accepted that the initiator decomposes in the continuous aqueous phase into primary free radicals and that the conversion of the monomer takes place mainly inside the colloidal particles. This process enables the production of very high molecular weight polymers at increased polymerization rates and is therefore of considerable industrial importance.[1] One of the most important issues in emulsion polymerization is the question how comes which kind of radical in the latex particles. Despite the technical importance of emulsion polymerization, there is in the open scientific literature only one report describing an attempt to experimentally determine directly the entry rate and to verify the nature of the entering radicals.[2] In a clever approach the authors decorated cross-linked polystyrene latex particles with 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy free radicals (TEMPO) and used them as seed particles in a subsequent polymerization of methyl methacrylate (MMA). The entry coefficient of methyl methacrylate oligomers into 86 nm sized seed particles was estimated to be 1.5 s^{-1} from the decay of the ESR signal at short polymerization times. The average chain length of the trapped oligomers was analyzed after thermolysis by size exclusion chromatography and determined to be about 5. The results of this study are considered as proof for an entry mechanism based on the assumption that radicals born in the aqueous phase can enter latex particles only if they polymerize to a critical chain length j_{crit} supplying them with some surface activity as proposed in ref 3. Nowadays this entry mechanism based on the control by oligomer growth in the aqueous phase is commonly accepted to be valid for emulsion polymerization. It is frequently used to evaluate kinetic polymerization data, basically the rate of polymerization in seeded polymerization, by more or less appropriate models and appears to be correct; cf. a recent example given in ref 4. However, unambiguous experimental proof that only oligomeric radicals and not also primary initiator radicals enter the latex particles has not been given so far. Even the above-mentioned experimental results[2] do not supply this evidence as only carbon-centered radicals are trapped by TEMPO, but peroxyl radicals oxidize the *N*-oxide without being thermoreversibly trapped.[5] Moreover, as the TEMPO molecules were coupled to acrylic acid units, they were located rather in an outer shell than in the interior of the particles, and hence, they trapped radicals in the vicinity of the particles.

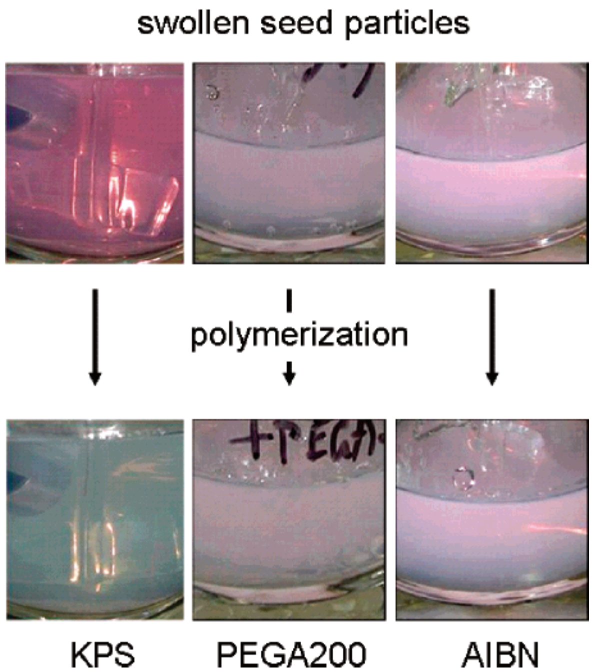

Figure 1. Photographs of the reaction mixtures before the start of seeded RAFT emulsion polymerizations (upper row) and at the end of the reactions (lower row) illustrating the effect of different primary initiator radicals on the preservation of the RAFT agent inside the seed particles.[7]

We report here direct experimental evidence without any ambiguous assumptions or model affected data interpretation that during emulsion polymerization primary initiator radicals enter the latex particles and start reactions therein. The following experimental study is based on observations made during an investigation of seeded emulsion polymerization in the presence of reversible addition fragmentation chain transfer (RAFT) agents, which are used to control radical polymerization via the RAFT process.[6] Latex particles containing benzyl dithiobenzoate (BDB) or 1-phenylethyl dithiobenzoate (PhEDB) RAFT agents are reddish colored. During the seeded polymerization started with potassium peroxodisulfate (KPS) a fast decoloration of the dispersion was observed whereas during polymerizations started with azo-initiators (2,2′-azobis(isobutyronitrile), or PEGA200, which is a 2,2′-azodi(poly(ethylene glycol) isobutyrate) with a molecular weight of the poly(ethylene glycol) chains of 200 g/mol) the color faded much slower, and the dispersions were still dyed at the end of the polymerization (cf. Figure 1). This qualitative result must be considered as direct proof that primary radicals enter the seed particles and that in the case of KPS as initiator the strongly oxidizing sulfate ion radicals cause the bleaching due to side oxidation reactions as was also observed for the TEMPO decorated particles described in ref 2.

The water solubility of the RAFT agents BDB and PhEDB is less than that of styrene as it was impossible to detect them in the aqueous phase by UV−vis spectroscopy even if cuvettes with 5 cm optical path length were used. Also, these compounds should not show any surface activity under the particular conditions as their interfacial tension to water should be comparable with that of either ethylbenzene or styrene, and hence, their

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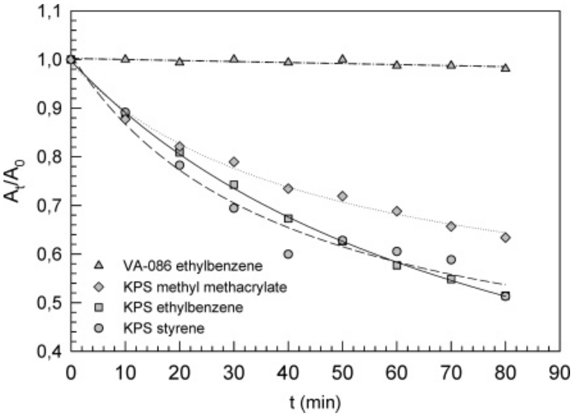

Figure 2. Relative change of the absorbance at 502 nm during the initiator decomposition (KPS or VA-086) in the presence of polystyrene seed latex (unswollen particle diameter 35 nm) swollen with BDB solution in methyl methacrylate, or ethylbenzene, or styrene; A_0 is the absorbance of the swollen particles before initiator addition, and A_t is the absorbance at time t after initiator addition.[9]

concentration at the interface should correspond to their number fraction inside the particles.

To quantify this observation, the reaction was followed by in-line UV−vis spectroscopy as described recently in ref 8. The most important experimental data for the following conclusions are summarized in Figure 2 and show clearly the difference between both initiator types (KPS and 2,2′-azobis(2-methyl-*N*-(2-hydroxyethyl)propionamide) (VA-086)). For this experiment VA-086 was chosen as azo-initiator because it is water-soluble at neutral pH, it has a higher water solubility than PEGA200, and it can be applied as aqueous solution in the same way as KPS. Before initiator addition at time zero the latex particles were swollen with a BDB solution either in monomer (styrene or MMA) or in an inert solvent (ethylbenzene). The applied amount of RAFT agent solution was lower than the necessary amount for equilibrium swelling of the latex particles. Hence, the situation before adding initiator solution corresponds to the monomer starvation period during the third stage of a batch emulsion polymerization.

This condition ensures that no free monomer phase is present, and BDB is located almost quantitatively inside the latex particles as its water solubility is so low that it was not possible to detect even traces in water with UV−vis spectroscopy. In comparison, for experiments in the absence of latex particles no absorption was measured in the BDB absorption range between 420 and 570 nm.

During all the experiments with KPS the absorbance in the range of the RAFT agent rapidly decreases regardless of whether the dispersion contains monomer or ethylbenzene. If a monomer is present, the absorbance immediately after initiator addition changes not only due to the degradation of the RAFT agent but is also influenced by the polymerization reaction, which can cause increasing turbidity. Contrarily, for VA-086 in the absence of monomer the absorbance decreases within the first 90 min after initiator addition by only 2%.

The UV−vis data in Figure 2 undoubtedly reveal two important results without any special knowledge about the mechanism of emulsion polymerization. First, the comparison of the two data sets with ethylbenzene as inert solvent clearly shows that sulfate ion radicals decolorize BDB-containing polystyrene particles much faster than carbon-centered radicals. Although the particular mechanism is not clear, a side oxidation reaction is more likely due to the high redox potential of 2.6 eV of the sulfate ion radical[10] than an exchange of the benzyl group of the BDB. Moreover, several examples are known for oxidation reaction of organic sulfur compounds by persulfate.[11] An evaluation of the data in Figure 2 for the combination KPS/ethylbenzene, which is not influenced by polymerization and hence the fastest fading of the red color of the particles is observed, as first-order reaction results in a reaction rate constant of 2.80×10^{-5} s^{-1}. This value is pretty close to the decomposition rate constant for KPS at 70 °C, which is 2.2×10^{-5} s^{-1} as given in ref 12. In contrast, for the combination VA-086/ethylbenzene the first-order reaction rate constant is almost 2 orders of magnitude lower (5.54×10^{-7} s^{-1}) and also much less than the decomposition rate constant of the initiator, which is about 4×10^{-6} s^{-1}at 70 °C.[13] This first result is of special meaning for controlled radical emulsion polymerizations with RAFT as it proves the possibility of the degradation of RAFT agents by peroxide radicals not only in the water phase but also inside the hydrophobic environment of latex particles. Contrarily, azo-initiators contribute obviously mainly to the initialization of the RAFT process[14] and side oxidation reactions, which can occur if oxygen is not completely excluded are only of minor importance.[15] This result does not mean that control with RAFT agents in peroxodisulfate-initiated emulsion or miniemulsion polymerization is not possible. Despite the here observed degradation of the RAFT agent and all the other problems as discussed in ref 16, a certain degree of control can be achieved in ab initio and seeded emulsion polymerizations with peroxodisulfate as initiator. Compared with "normal" emulsion polymerizations, the experiments carried out in this study favor reactions between peroxodisulfate radical ions and RAFT agent molecules as both the average particle size and the monomer concentration inside the particles are lower than usual. Consequently, especially the concentration ratios of monomer to RAFT agent and of RAFT agent to sulfate ion radicals are lower than under "normal" emulsion and miniemulsion polymerization conditions. Indeed, results are published describing the successful application of RAFT in emulsion[17−21] and miniemulsion[22] polymerizations initiated with sodium or potassium peroxodisulfate. As the main focus of these papers was the investigation of the molecular weight control, no attention was paid to the fate of the RAFT agent. Only in ref 20 did the authors report on side oxidation reaction between the dithio RAFT agent and persulfate in the aqueous phase leading to CO_2, CS_2, and other organic products.

Second, the comparison of all reactions with KPS unambiguously shows that sulfate ion radicals enter the particles in any case, even if monomer is present, as the initial decay for all three curves is identical within the experimental error. The slower decrease in the relative absorbance with MMA as solvent and monomer at longer reaction times might be caused by at least two reasons. First, an increased consumption of initiator radicals in aqueous phase reactions due to the much higher water solubility of methyl methacrylate compared with styrene[16] reduces the number of sulfate ion radicals able to enter. Second, the concentration of oligomeric radicals with $j > 1$ in the water phase is increased, and hence carbon-centered radicals might enter and react with BDB via the normal exchange reaction, which does not cause decoloration. The meaning of this second result for the understanding of emulsion polymerization is enormous as it shows that the commonly accepted entry mechanism of radicals has to be revised and the entry of primary initiator radicals has to be considered. There is obviously no preference of the particles to allow only a special sort of radicals to enter, which are either primary or oligomeric radicals. Contrarily, the results allow the conclusion that any kind of radical, which is present in the aqueous phase, can enter the particles obviously with a probability proportional to its concentration. Moreover, the generalization of these results leads to the argumentation that not only radicals but also initiator molecules or any other type of molecule present in the aqueous phase can enter the particles. On the basis of the results presented here, it is not possible to exclude that initiator molecules come into the particles and decompose there. In this sense latex particles should be considered as rather unspecific sorbent phase as was recently proven by our group.[8]

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(7) All seeded polymerizations were carried out at in the absence of a free monomer phase at 70 °C until complete conversion. For KPS the polystyrene seed latex was swollen with a solution of BDB in styrene. The polymerizations with PEGA200 and AIBN were carried out with poly(methyl methacrylate) seed latexes swollen with PhEDB solution in styrene. To start the polymerizations, aqueous and methanolic solutions of KPS or PEGA200 and AIBN were added after equilibration of the reaction mixture.

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(9) A 250 mL all-glass reactor equipped with condenser, stirrer, heating and cooling jacket, and 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. The reactor was filled with 200 g of polystyrene dispersion containing particles of an average diameter of 35 nm and a 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. To achieve a complete uptake of the organic phase during the sorption experiments, a solution of 2×10^{-4} mol of BDB in either 0.74 g of styrene, or 0.77 g of methyl methacrylate, or 0.71 g of ethylbenzene was placed on top of the dispersion inside the reactor. Before depositing the solution the dispersion was heated to 70 °C, and the absorption baseline was measured after thermal equilibration and before adding the initiator (43 mg of KPS or 46 mg of VA-086 dissolved in 2 g of water).

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