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Calorimetric study on the influence of the nature of the RAFT agent and the initiator in ab initio aqueous heterophase polymerization

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Abstract

Experimental results regarding reaction rate profiles and final latex and polymer properties are presented for combinations of four different RAFT agents [benzyl dithioacetate (BDA), benzyl dithiobenzoate (BDB), 1-phenyl ethyl dithiobenzoate (PhEDB), and cumyl dithiobenzoate (CDB)] and three types of initiators [potassium peroxodisulfate (KPS), 4,4′-azobis (4-cyanopentanoic acid) (ACPA), and poly(ethylene glycol)-azo-initiator (PEGA200)]. It was found out that at given type of RAFT agent the type of initiator has a strong influence on the reaction rate profiles as well as on both the molecular properties of the polymers and the colloidal properties of the latexes. Among the RAFT agents tested BDA is the most efficient one regarding the control of chain growth.

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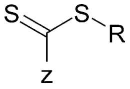
Keywords: Reaction calorimetry; Heterophase polymerization; RAFT

1. Introduction

Controlled radical polymerization (CRP) has become one of the most rapidly growing topics in the field of polymer research in the last decade of the 20th century [1,2]. The use of CRP strategies in aqueous heterophase polymerization techniques is nowadays an actual topic of polymer research as it promises to be potentially of enormous practical importance [3–5].

Among the strategies to control radical polymerizations the method of reversible addition-fragmentation chain transfer (RAFT) is due to its versatility and effectiveness widely used [6–21]. The experimental and theoretical studies of various groups points out that for the polymerizations employing thiocarbonylthio compounds (Formula 1) as RAFT agent the results are strongly dependent on the nature of the activating group Z and the leaving group R [7,9].



Formula 1

However, the performance of the R and Z groups in an aqueous dispersed system might not be the same as in bulk or solution since the water solubility of these groups as well as their partition between the different phases plays an important role, cf. [22,16]. On the other hand, it has been shown that the nature of the initiator influences both the molecular properties of the polymers (molecular weight distribution) and the colloidal properties of the latexes (particle size distribution and colloidal stability) made by heterophase polymerization [23]. It can be expected that in the case of heterophase polymerizations in the presence of RAFT agents the overall scenario is even more complicated as the solubility of the RAFT agent and particularly that of the leaving and activating group in the continuous phase strongly influences the effectiveness of the control.

The aim of this contribution is to present the results of a comprehensive experimental study on the influence of the nature of both the initiator and the RAFT agent on the reaction rate and the final latex properties by means of reaction calorimetry of batchwise ab initio emulsion polymerization of styrene. This study comprises four

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RAFT agents with leaving and activating groups of different solubility in water and three basically hydrophilic azo- and peroxo-initiators but with different partition behavior among the various reaction loci. It is to emphasize that reaction calorimetry does not allow continuous sampling at fixed time intervals and thus, the reaction rate profiles of the whole course of the polymerization and properties of the final latexes are discussed.

2. Experimental

2.1. Materials

The water was taken from a Seral purification system (PURELAB Plus™) with a conductivity of 0.06 μs cm^{-1} and degassed prior to use for the polymerization. Styrene (Aldrich) was distilled under reduced pressure to remove inhibitors. Initiators potassium peroxodisulfate (KPS) and 4,4′-azobis(4-cyanopentanoic acid) (ACPA) (Fluka) and surfactant, sodium dodecyl sulfate (SDS) (Roth) were used as received. Poly(ethylene glycol)-azo-initiator (PEGA200) with an average molecular weight of 568 g/mol was synthesized as described elsewhere [24]. RAFT agents benzyl dithioacetate (BDA), benzyl dithiobenzoate (BDB), 1-phenyl ethyl dithiobenzoate (PhEDB), and cumyl dithiobenzoate (CDB) were synthesized and characterized in the lab according to literature description [25].

2.2. Polymerization

For all combinations of initiator and RAFT agent the following standard recipe was used: 80 g of water, 4 g of aqueous sodium dodecyl sulfate solution (5-wt%), 20 g of styrene monomer, 4.26×10^{-4} mol of RAFT agent, and 3.41×10^{-4} mol of initiator. The polymerization reactions were carried out batchwise at 80 °C in a pre-calibrated reaction calorimeter CPA 200 from ChemiSens (Lund, Sweden) with a 200 ml reactor equipped with a stainless steel stirrer and a heating facility through the reactor bottom. Nitrogen was purged into the reactor containing 70 g of water and the SDS solution, after 30 min styrene (containing the RAFT agent, degassed) was added. In the case of ACPA as initiator the pH was adjusted to basic conditions by adding 235 mg of aqueous ammonia solution (25 wt%). Then the reactor was closed and placed in the heating bath and the initiator solution (the corresponding amount dissolved in 10 g water) was injected into the reactor after the temperature equilibration. The directly resulting output of the reaction calorimetry is a heat flow–time curve corresponding to a polymerization rate–time curve or reaction rate profile [26].

For the chain extension experiments the combination KPS/BDA was used and styrene as monomer in the first stage. After the finishing of heat formation another batch of monomer either 10 g of styrene or BMA was added and the polymerization was continued until completion.

After the polymerizations and before any characterization of the latexes the coagulum was removed by passing the dispersion through a pore one sintered glass frit. Consequently, the solids content are not only a measure of the conversion but corresponds much more inversely to the amount of coagulum formed during the polymerization. The theoretical solids content indicating coagulum-free polymerization is between 19.5 and 19.7 depending on the type of initiator and RAFT agent. The lowest and the highest solids content for all investigated systems after filtration, was obtained for the combination KPS/BDA and KPS alone with 17.7 ± 1.8 and 19.4 ± 0.5%, respectively. The highest value in the presence of RAFT agent is obtained for the combination ACPA/PhEDB with 19.3 ± 1.2% indicating practically coagulum free polymerization and almost complete conversion.

In order to simplify the comparison of the results for all RAFT agent–initiator combinations (Fig. 2) a single value was assigned to each curve as an average rate of polymerization. First, the conversion-time curve was calculated from the integrated heat flow–time curves between initiator addition ($t=0$) and the time when the heat flow reaches again zero. Then, the slope between about 10 and 80% conversion was calculated. This value (multiplied by a factor 1000 to get numbers in a convenient order of magnitude) is used as 'average' reaction rate. With this procedure on the one hand one can compare polymerizations possessing different rate profiles and on the other hand the effect of inhibition periods observed in some of the reactions is eliminated. It is to admit that although some conclusion can be drawn (cf. below) this is a rough procedure as not all information included in the rate profiles are considered.

2.3. Characterizations

Samples were taken at the end of all the polymerizations and the latexes were characterized regarding solids content with a HR73 Halogen Moisture Analyzer (Mettler Toledo) and average particle size (intensity weighted diameter) with a Nicomp particle sizer (model 370, PSS Santa Barbara, USA) at a fixed scattering angle of 90°. To isolate the polymer a few drops of latex were instilled into an excess amount of petroleum ether and the precipitated polymer was separated and dried. 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 ultra violet (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

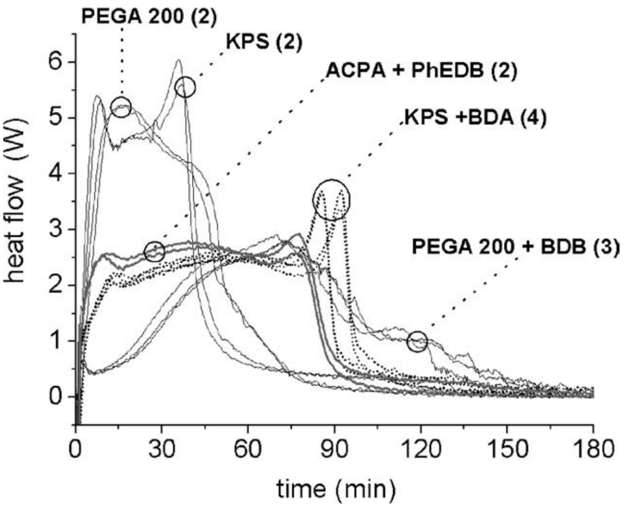


Fig. 1. Reaction rate profiles as obtained directly by reaction calorimetry of ab initio emulsion polymerization of styrene at 80 °C in presence of various RAFT agents and initiators, (the numbers in the parenthesis refer to the number of repeats).

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 standards (between 500 and 2×10^6 g mol^{-1} from PSS, Mainz, Germany).

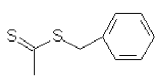
From the solids content and the content of auxiliary materials the polymer content was calculated (PC). The ratio between experimental and theoretical PC corresponds to the conversion of monomer to latex (not considering the coagulum), which together with the number average molecular weight is used to calculate the number of polymer chains (N_c).

2.4. Reproducibility of the experimental techniques

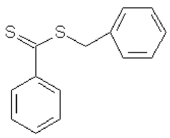
The data summarized in Fig. 1 show exemplarily the reproducibility of the calorimetric procedure employed. As

Table 1

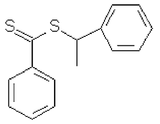
(a) RAFT agents:



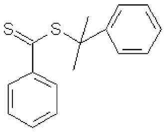
Benzyl dithioacetate (**BDA**)



Benzyl dithiobenzoate (**BDB**)

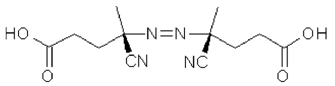


1-Phenylethyl dithiobenzoate (**PhEDB**)

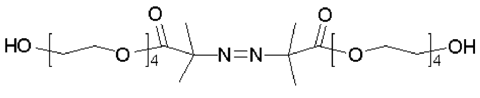


Cumyl dithiobenzoate (**CDB**)

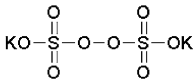
(b) Initiators:



4,4'-azobis (4-cyanopentanoic acid) (**ACPA**)



poly (ethylene glycol)-azo-initiator (**PEGA 200**)



potassium peroxodisulfate (**KPS**)

it can be seen the reproducibility is sufficiently good also for discussing the shape of the reaction rate profiles in dependence on the RAFT agent–initiator combination.

Both the reproducibility of the calorimeter runs and the consistency of the data treatment are proven by the overall values of the heats of polymerizations (ΔH_{pm}). For all polymerizations considered in this study the average value obtained by integration as described above is $\Delta H_{\mathrm{pm}} = 70.5 \pm 2\ \mathrm{kJ\ mol^{-1}}$. This value lies in between published values by Dainton et al. (74.1 ± 2.9 and $68.7 \pm 1.3\ \mathrm{kJ\ mol^{-1}}$) [27]. This average value indicates that all polymerizations have been carried out to almost complete conversion.

The analysis of the latex and polymer from repeated polymerization experiments has shown that the reproducibility of both the average particle size with the Nicomp and the average molecular weights with the GPC equipment is better than ±5%.

3. Results and discussion

For the following discussion it is necessary to emphasize that the results were obtained in batch ab initio emulsion polymerizations. This means that the starting monomer in water emulsion converts after periods of particle nucleation and particle growth into the final latex. Thus, the partition of the RAFT agents between the monomer droplets and the monomer swollen latex particles and the monomer saturated continuous aqueous phase is crucial. This is a very important difference compared with suspension, miniemulsion, or seeded heterophase polymerization where the major part of the reaction takes place inside preformed emulsion droplets (a monomer swollen seed particle behaves effectively as an emulsion droplet) where also the major part of the hydrophobic RAFT agents is located.

The chemical structure of the employed RAFT agents and initiators are listed in Table 1.

The RAFT agents CDB, PhEDB, and BDB can be considered as homologous series as all have a phenyl group as their activating (Z) group and their leaving (R) group only differs in the number of methyl groups. Therefore, these RAFT agents are expected to slightly differ in their water solubility in the order of BDB > PhEDB > CDB. Consequently, their R groups that are benzyl, phenylethyl (2-phenylethyl with the radical-function at the 2-carbon of the ethyl group), and cumyl (2-phenylpropyl with the

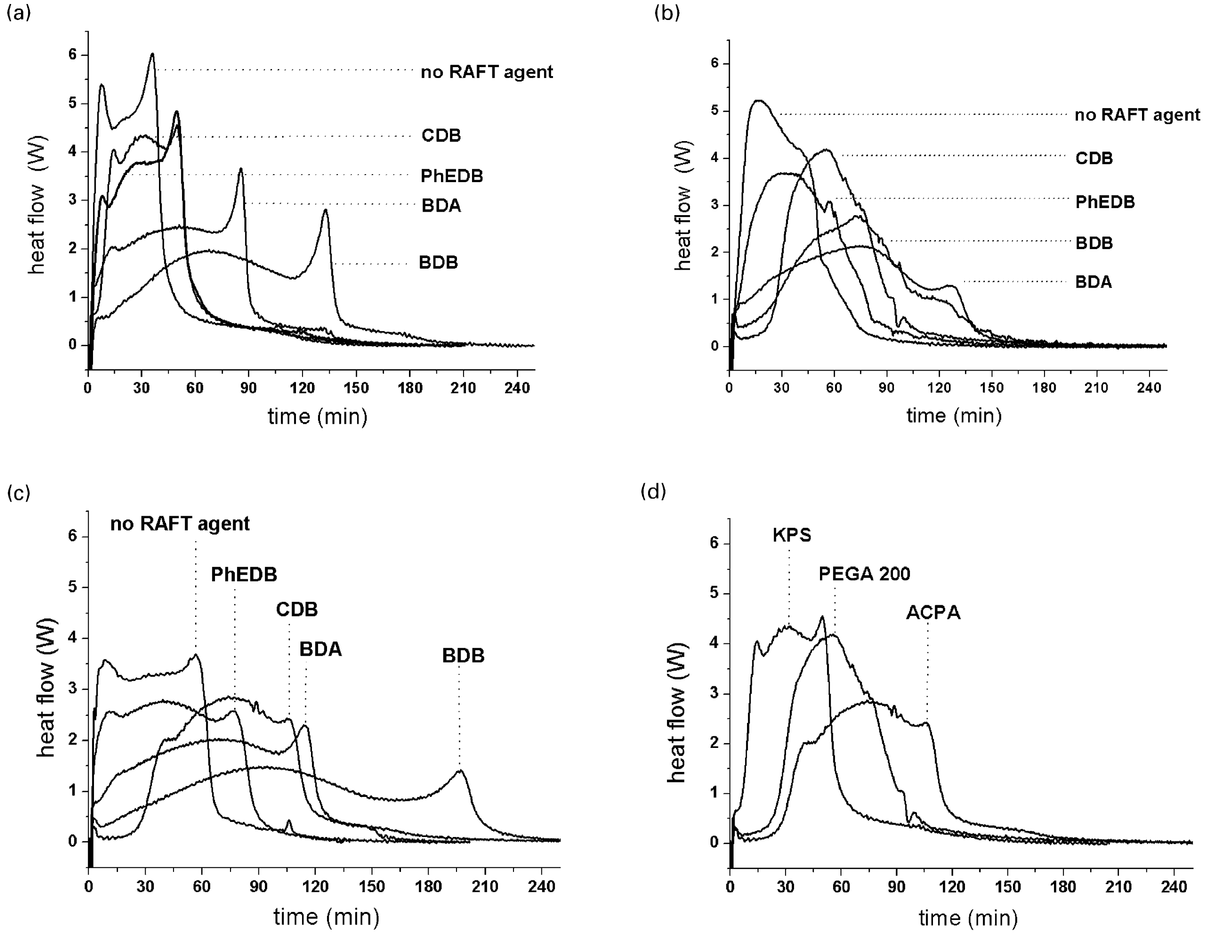


Fig. 2. Reaction rate profiles as obtained directly by reaction calorimetry of ab initio emulsion polymerization of styrene at 80 °C in presence of various RAFT agents initiated with (a) KPS, (b) PEGA200, (c) ACPA, and (d) all three initiators for RAFT agent CDB.

radical-function at the 2-carbon of the propyl group) radical, respectively, are expected to have different water solubility and re-initiation capability. BDA and BDB have the same leaving group but different activating groups (methyl and benzyl, respectively) with different water solubilities (methyl higher than benzyl). Although no solubility data are presently available it is fair to expect that among these RAFT agents BDA is the most hydrophilic one and CDB is the most hydrophobic one.

The water solubility of the initiating primary radicals descended from the initiators should vary in the following order: sulfate ion radical (from KPS) $>1,1'$-cyano methyl butyric acid with the radical function at the 1-carbon atom (from ACPA) $>$ 2-carbonyl oxy poly(ethylene glycol) with the radical function at the 2-carbon of the propyl group (from PEGA200).

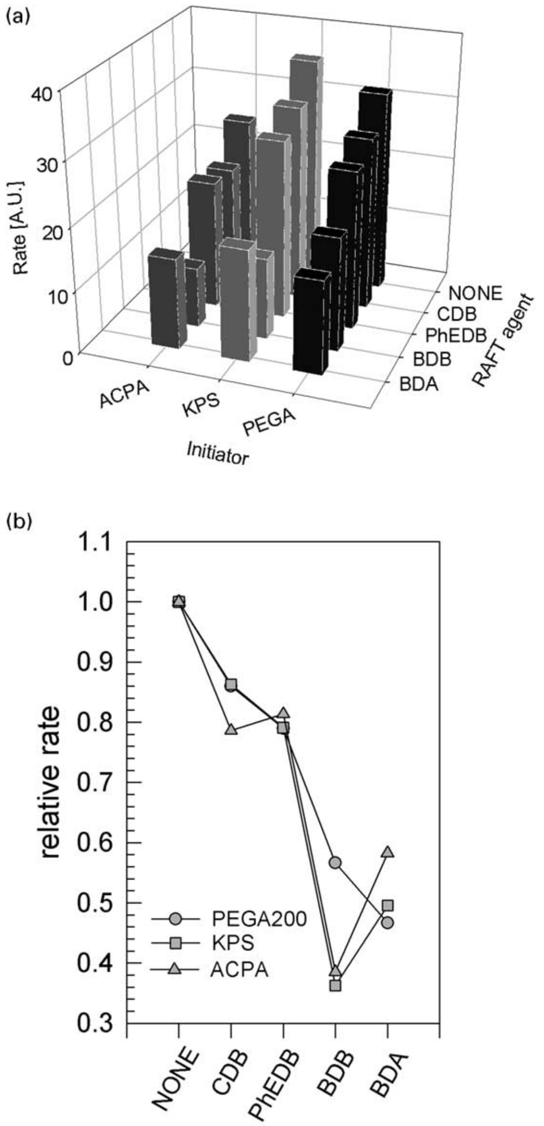


Fig. 3. (a) Average polymerization rates of ab initio emulsion polymerization of styrene at 80 °C with various RAFT agent–initiator combinations. (b) Average rate normalized relative to the rate obtained in the absence of RAFT agents for each type of initiator.

For the polymerizations with ACPA the pH of the continuous phase was basic in order to ensure complete dissolution. The situation regarding PEGA200 is more complex as poly(ethylene glycol) is soluble in both the water and the monomer phase; however, the partition coefficient depends on the temperature [28].

The nature of the RAFT agent has indeed a strong influence on the polymerization rate at a given initiator as it is illustrated by the data put together in Fig. 2(a)–(c). There is a tendency to recognize that the polymerization rate changes only slightly if hydrophobic RAFT agents such as CDB are employed. Contrary, the polymerization considerably slows down for RAFT agents with increasing hydrophilicity such as BDB and BDA. However, it is also obvious that the general shape of the rate profile is basically determined by the nature of the initiator; and moreover, the presence of any of the RAFT agents decelerates the polymerization reaction (the rate profiles are stretched along the *X*-axis and depressed along the *Y*-axis).

The following experimental facts clearly underline the complexity of the interaction between free radical initiators and RAFT agents in aqueous heterophase polymerizations. For instance, the sequence of the deceleration of the polymerization rates as obtained for KPS (Fig. 2(a)): BDB $<$ BDA $<$ PhEDB $<$ CDB, for PEGA 200 (Fig. 2(b)): BDA $<$ BDB $<$ PhEDB $<$ CDB, and for ACPA (Fig. 2(c)): BDB $<$ BDA $<$ CDB $<$ PhEDB points to more than a simple influence of the water solubility of the RAFT agents.

It is to note, that the reaction rate profiles for the pure initiators depicted in Fig. 2(a)–(c) show that the different decomposition rates of the initiators are obviously only of minor importance compared with the influence of the RAFT agents. For a better evaluation of the deceleration effect Fig. 3(a) and (b) compares the average rates of polymerizations (cf. Section 2).

The general experimental observation that the more hydrophilic RAFT agents (BDB, BDA) cause a stronger deceleration than the more hydrophobic ones (PhEDB, CDB) confirms the importance of the continuous aqueous phase for heterophase polymerization kinetics in particular for the radical generation and radical exchange processes with the particles. It is to mention that also Monteiro et al. [29] observed lower polymerization rates for RAFT agents with more hydrophilic leaving groups. Despite the particular mechanism the experimental data presented here on the one hand clearly indicate that the water solubility of the leaving group has a strong influence on the magnitude of the deceleration. On the other hand these data underline the importance of the reactions in the continuous phase.

A closer look at the data summarized in Fig. 3(a) and (b) reveals that the proportionality between the rate deceleration and the water solubility of the RAFT agents only holds for PEGA200 as initiator. This is interesting as among the employed initiators PEGA200 is the only one acting in all

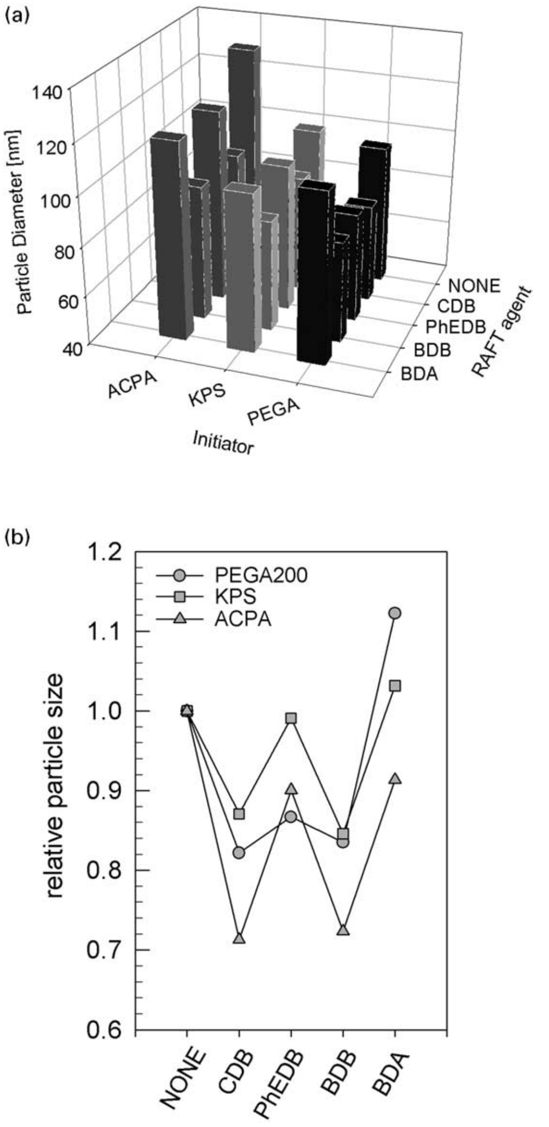


Fig. 4. (a) Average particle size of latexes obtained in ab initio emulsion polymerization of styrene at 80 °C in the presence of various RAFT agents initiated with different initiators. (b) Average particle size normalized relative to the size obtained in the absence of RAFT agents for each type of initiator.

three phases of a heterophase polymerization, which are the continuous phase, the particle phase, and the interface. For ACPA and KPS, acting mainly in the continuous phase and only partly at the interface, an increase in the average rate is observed for the more hydrophilic BDA in comparison to BDB.

Moreover, the data put together in Fig. 2(d) show that for a given RAFT agent (here exemplary CDB) the polymerization rate profiles are strongly influenced by the nature of the primary free radicals. Another experimental fact revealed by the data in Fig. 2(d) is the occurrence of an initial retardation period after initiator injection. This is especially pronounced for CDB as RAFT agent. The duration of this strong retardation period depends on the nature of the initiator, as it is about 5 min for KPS, about 20 min for PEGA200, and almost 30 min for ACPA. A strong retardation period in the presence of CDB as RAFT agent has also been observed by other groups in bulk and solution but also miniemulsion polymerizations [12,15,18,17]. Exemplary, Prescott et al. [17] observed even inhibition periods between 45 min and 3 h also for a RAFT agent with cumyl as leaving radical and with benzyl activating group. The mechanistic reason for this behavior of RAFT agents with cumyl radicals as leaving group is still unclear and a matter of intense discussion [12,15,18,17]. However, on the base of the presented results one can very likely exclude an influence of the activating group as BDB, PhEDB, and CDB have the same Z group and a distinct inhibition period was only observed for CDB. Likewise an influence of the intermediate species formed with polymeric radicals can be excluded. It seems based on the presented results much more likely that this strong retardation period is caused by a slow re-initiation capability of the cumyl radical, especially, under the conditions of aqueous heterophase polymerizations. However, another possible reason, which cannot be omitted by these experimental results, might be a slow fragmentation of the R group after the first addition reaction, cf. [30,31].

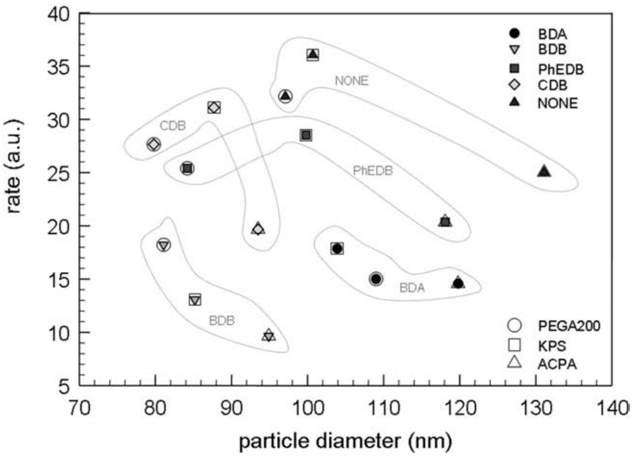


Fig. 5. Average rate of polymerization versus average particle diameter for polystyrene latexes prepared by ab initio emulsion polymerization in the presence of various RAFT agents and initiators (open symbols: initiators; filled symbols: RAFT agents).

There is also a distinct influence of the nature of the RAFT agent on the average particle size of the final latexes as illustrated in Fig. 4(a) and (b). Interestingly for each initiator the average particle size changes with the same pattern when the water solubility of the RAFT agents increases. This W-shaped pattern underlines the enormous influence of the nature of the RAFT agent also on the colloidal properties during aqueous heterophase polymerizations. This influence even seems to override the influence of the initiator on the average particle size. However, an overall comparison (cf. Fig. 4(a)) shows that for all the

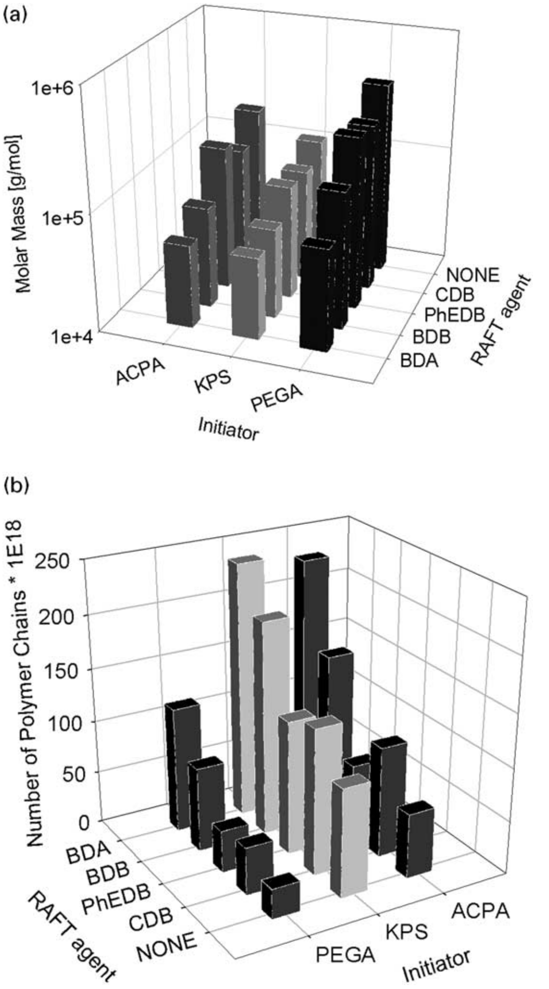


Fig. 6. (a) Number average molecular weight (M_n, cumulative) (b) and average number of chains (N_c, cumulative) of the polymers prepared by ab initio emulsion polymerization of styrene at 80 °C in the presence of various RAFT agents and initiators.

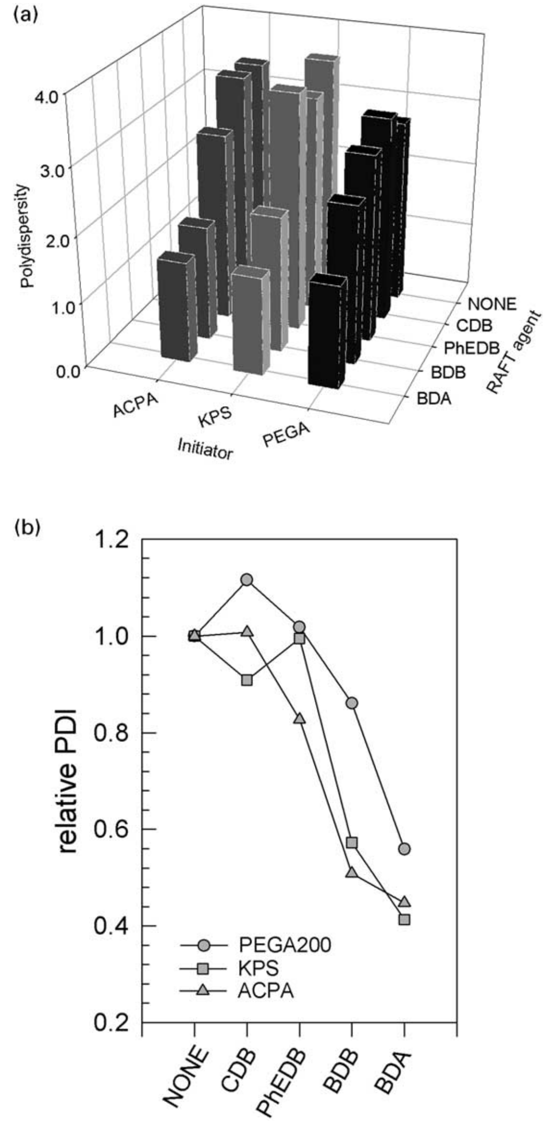


Fig. 7. (a) PDI of the molecular weight distribution for ab initio emulsion polymerization of styrene at 80 °C in the presence of various RAFT agents initiated with different initiators. (b) PDI for each type of initiator normalized relative to the value obtained in the absence of RAFT agents, which is 2.82, 3.64, and 3.45 for PEGA 200, KPS, and ACPA, respectively.

RAFT agents except BDA, the smallest particles were obtained when PEGA200 was used as initiator as it was also observed in the absence of RAFT agents [23].

It is an inherent feature of heterophase polymerizations that the polymerization kinetics and also the rate of polymerization depend on the average particle size. Generally, the polymerization is faster the smaller the average particle size. The data summarized in Fig. 5 reveal that this is also the case for the polymerizations considered here although the relation is expectedly influenced by the nature of the RAFT agent. For example, polymerizations with CDB and BDB result in similar particle sizes but different rates for the same type of initiator and BDA and BDB lead to similar average polymerization rates but different particle sizes.

The main task of RAFT agents is to control the molecular weight and to enable sequential growth steps during radical polymerization. This ability of a RAFT agent can be evaluated by means of the evolution of the average molecular weight with increasing conversion, the number of polymer chains formed, the polydispersity index of the molecular weight distribution, and the possibility of chain extension or block copolymer formation. Due to the particular condition of the reaction calorimetry continuous sampling was impossible and hence, the subsequent discussion is limited to the values obtained for the final latexes and to chain extension experiments. If the total number of chains is close to the theoretical value the RAFT agent and the whole process can be considered as effective. For the particular conditions employed in this study the theoretical number average molecular weight and the theoretical total number of chains are 4.69×10^4 g/mol and 2.57×10^{20} chains, respectively. These numbers were estimated according to standard relation, cf. [3], taking into

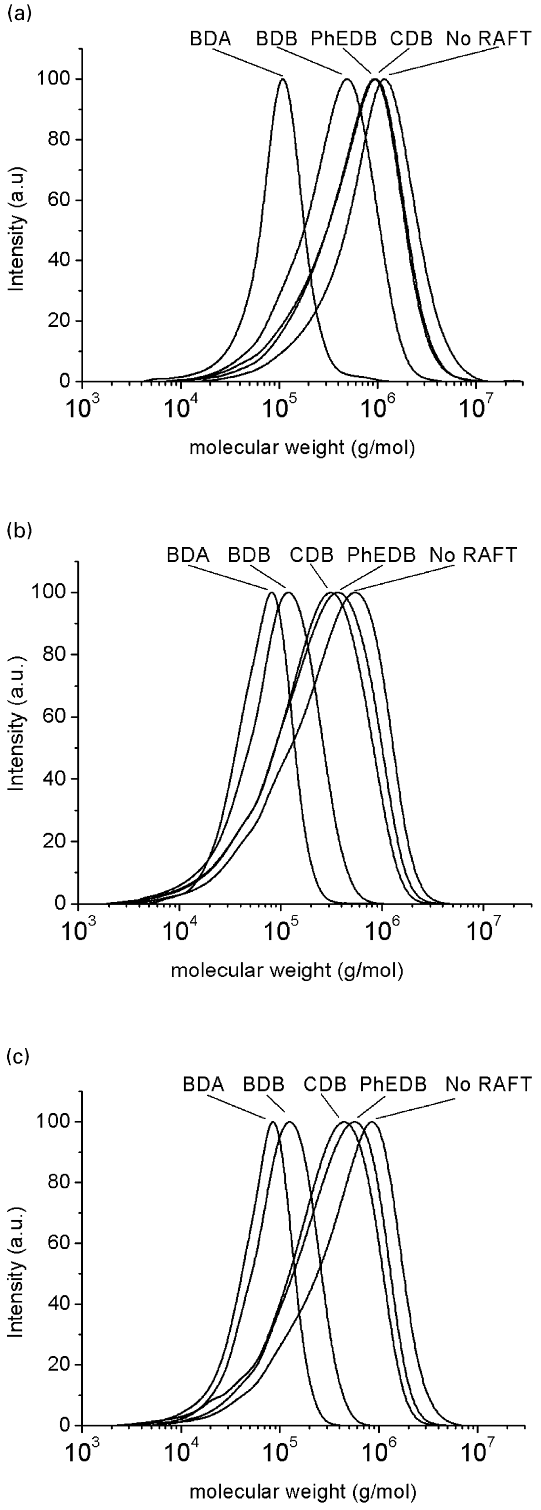


Fig. 8. Influence of the RAFT agent on the molecular weight distributions for ab initio emulsion polymerization of styrene at 80 °C initiated with different initiators (a) PEGA 200, (b) KPS, and (c) ACPA.

account only the overall concentration of RAFT agent and assuming complete monomer conversion. The influence of the nature of the RAFT agent on both the number average cumulative molecular weight and the number of chains formed is demonstrated by the data depicted in Fig. 6(a) and (b), respectively.

These data show both an increasing number of chains and a decreasing average molecular weight with increasing water-solubility of the RAFT agent. The fact, that the more water soluble KPS and ACPA lead to a higher number of polymer chains than PEGA200, is another experimental hint regarding the importance of the aqueous phase as reaction locus. The data of the polymerization rates as depicted in Figs. 2 and 3 are consistent with the M_n and N_c values in Fig. 6(a) and (b), respectively. Also the polydispersity indexes (PDI) of the molecular weight distributions, which denotes the ratio between the cumulative weight and number average molecular weights (Fig. 7) lead to the conclusion that BDA is the most effective RAFT agent for all types of initiators as it causes the narrowest molecular weight distributions.

Evaluating these data it is necessary to remind that especially for ab initio emulsion polymerizations procedures the PDI is usually larger than for solution or bulk polymerizations as a consequence of the different reaction loci (continuous phase, particle, and interface) which are quite different regarding the monomer concentration. The most hydrophobic RAFT agent, CDB, shows the least capability of control and the PDI values for PEGA200 and ACPA are even larger compared with RAFT agent-free polymerizations (Fig. 7(b)). The poor results obtained with CDB are in clear contradiction to bulk polymerizations of styrene where PDI values smaller than 1.2 have been obtained, cf. [6,9]. This comparison again underlines the peculiarities of RAFT processes under the conditions of aqueous heterophase polymerizations.

The PDI data prove that BDA is obviously among the investigated RAFT agents the compound of choice regarding control in ab initio aqueous emulsion polymerization of styrene. The molecular weight distributions as displayed in Fig. 8(a)–(c) verify this conclusion and moreover, give an impression on how the molecular weight distribution changes in the presence of different RAFT agents in comparison to the uncontrolled polymerizations.

In any single example given in Fig. 8 it is clear to see how the molecular weight shifts towards smaller values and how the skewness of the distribution changes with increasing

Table 2
Comparison of number average molecular weights and PDI values for ab initio emulsion polymerizations of styrene in the absence and presence of BDA with various initiators

Initiator/RAFT agent	M_n (g mol^{-1})	PDI
PEGA200/NONE	4.24×10^5	2.82
PEGA200/BDA	7.32×10^4	1.57
ACPA/NONE	1.88×10^5	3.45
ACPA/BDA	5.054×10^4	1.55
KPS/NONE	1.194×10^5	3.64
KPS/BDA	4.95×10^4	1.50

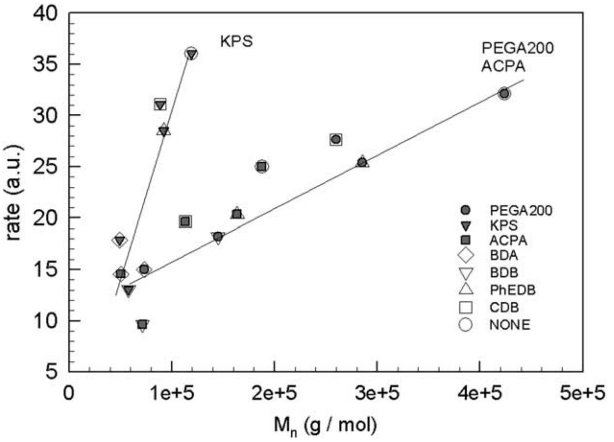


Fig. 9. Experimentally determined relation between the rate of polymerization and the average molecular weight for various RAFT agents and initiators employed; lines are only a visual guide.

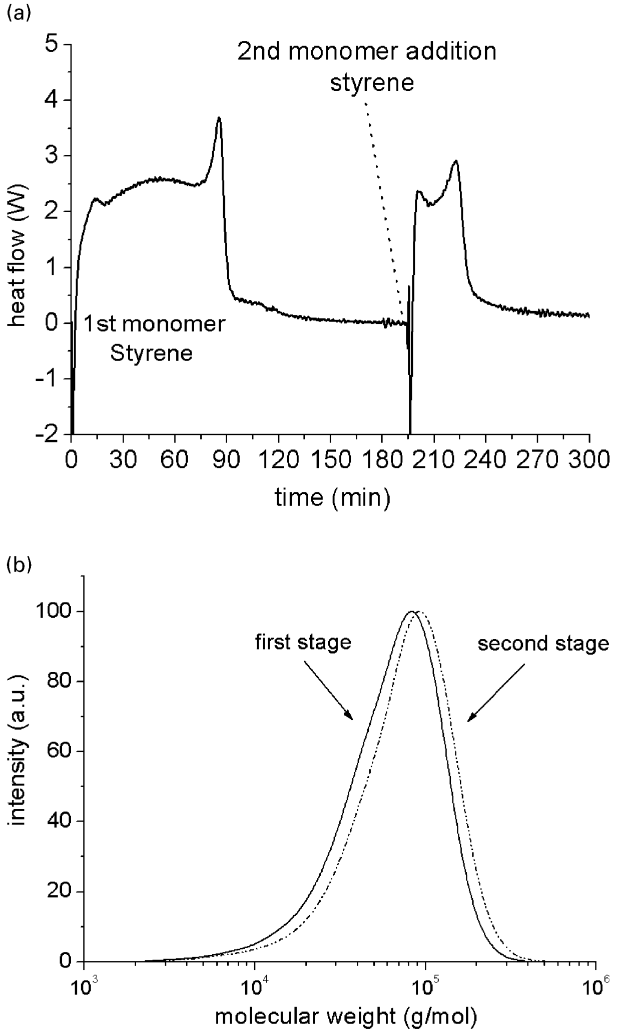


Fig. 10. Chain extension with styrene after finishing an ab initio emulsion polymerization of styrene at 80 °C with BDA as RAFT agent and KPS as initiator (a) calorimeter record (b) molecular weight distribution.

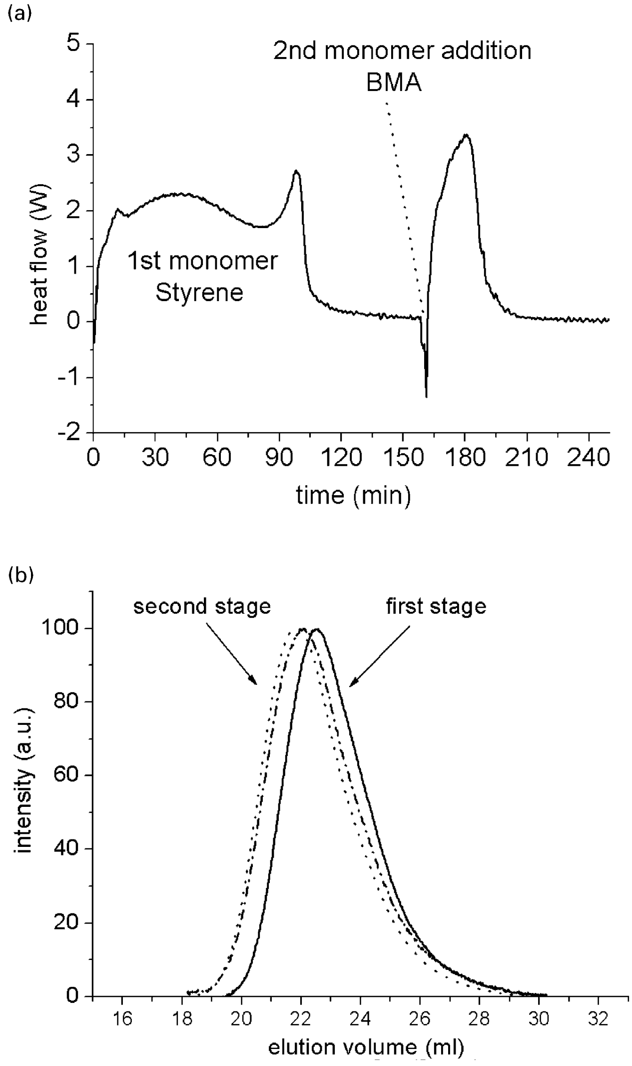


Fig. 11. Chain extension with BMA after finishing an ab initio emulsion polymerization of styrene at 80 °C with BDA as RAFT agent and KPS as initiator. (a) Calorimeter record (b) GPC trace (solid line: UV signal after first stage, dashed-dotted line: UV signal and dotted line: RI signal after second stage).

hydrophilicity of the RAFT agents. The presence of the RAFT agents does not change the order of the molecular weights as it is obtained in dependence on the kind of initiator also in the absence of RAFT agents. PEGA200 leads to the highest molecular weights followed by ACPA and then by KPS. Table 2 summarizes the data regarding average molecular weights and PDI values for BDA for all investigated initiators in comparison with the uncontrolled polymerizations.

The PDI of the molecular weight distributions for the uncontrolled polymerization shows a clear dependence on the nature of the initiator whereas it does not for the BDA-controlled samples. Despite the kind of initiator for BDA the PDI is in any case between 1.5 and 1.6. Moreover, the M_n value for the combination KPS/BDA is pretty close to the theoretical value which is 4.69×10^4 g/mol.

Since both the rate of polymerization and the average molecular weight in heterophase polymerization depend on the average particle size one might expect a relation between the average molecular weight and the average rate of polymerization as well. The data plotted together in Fig. 9 show that there is a positive relation between both average values. This is not really surprising for radical polymerizations with degradative chain transfer agents as their presence causes a decrease in both the rate and the molecular weight [32]. The surprising fact is the clear dependence on the nature of the thermo-labile group, which is almost independent of the nature of the RAFT agents. Potassium peroxodisulfate leads in comparison with the azo-initiators to lower molecular weights for given rate of polymerization. A possible reason for this might be the ability of peroxodisulfate to participate in side oxidation reactions. This difference is worth to mention since it underlines the important role of the type of initiator for radical polymerizations at least under the conditions of aqueous heterophase polymerizations independently whether RAFT agents are present or not.

The ability of chain extension and block copolymer formation in aqueous heterophase polymerization via RAFT agents under the particular conditions employed in this study was also proven. The experiments were carried out in the reaction calorimeter in the way that at the end of the polymerization, i.e. when the heat flow reached again the base line a second batch of monomer was added.

Exemplarily, Fig. 10(a) shows the calorimeter records for such polymerizations with styrene as second stage monomer (chain extension) and Fig. 11(a) gives an example for block copolymer formation with BMA as second stage monomer. The reaction rate profiles show that the second stage polymerization with styrene was not completed as the amount of heat detected is 5.8 kJ and about 1 kJ lower than the expected one. For the chain extension experiment with BMA the detected heat of polymerization indicates complete conversion as the heat of polymerization is with 65.4 kJ mol^{-1} higher than the value of 60 kJ mol^{-1} given in [27]. The solids content increases after the second stage polymerization in the expected range, i.e. up to values above 25%. Figs. 10(b) and 11(b) compare the molecular weight distributions and GPC traces, respectively, at the end of both stages. The GPC data confirm that chain extension was successful in both cases. Moreover, block copolymer formation took place to a certain extent, which can be concluded from the GPC traces depicted in Fig. 11(b) as the RI and UV signals cover with different intensities the same range of elution volumes. However, a closer look at the polymerization and molecular weight data for the chain extension experiment with styrene reveals that the number of chains increases during the second stage polymerization, which means that beside chain extension also formation of new chains occurred. The number and weight average molecular weight increased from 47 590 and 60 030 g mol^{-1} to 73 830 and 86 450 g mol^{-1}, respectively, and the PDI remained almost unchanged (1.60 versus 1.61). Regarding the quantification of block copolymer formation other techniques such as fractionation with selective solvents have to be applied.

4. Conclusion

The experimental data presented in this study show that the results of controlled radical ab initio emulsion polymerizations with RAFT agents depend not only on the kind of RAFT agent but also on the kind of initiator. Particularly, both the rate of polymerization and hence, the reactor efficiency as well as the range of molecular weights where control is possible can be optimized by choosing a proper combination of RAFT agent and free radical initiator.

The presented results show that for aqueous heterophase polymerizations of styrene the efficiency of molecular weight control is independently of the kind of hydrophilic initiator higher for more hydrophilic control agents such as BDA and BDB compared with more hydrophobic ones such as CDB and PhEDB.

Towards a better theoretical understanding of the experimentally observed dependencies more investigations including the development of the average particle size and the average molecular weight with polymerization time especially at the very beginning of the polymerization process are necessary. The initial period of the polymerization is of special importance as at this point the base for a successful control is laid.

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